CONTENTS

THE SOCIETY OF DYERS AND COLOURISTS
LONDON SECTION

THE SIXTH
LONDON LECTURE

COLOUR IN ART

by A. LUCAS Esq
Chief Restorer to the National Gallery

will be held at

THE WALDORF HOTEL
Aldwych   London WC2

at 7 pm on FRIDAY 24 OCTOBER 1958

A CORDIAL INVITATION IS EXTENDED TO ALL MEMBERS OF THE SOCIETY
AND THEIR FRIENDS

INTERNATIONAL FEDERATION OF ASSOCIATIONS OF TEXTILE CHEMISTS AND COLOURISTS

1959 INTERNATIONAL CONGRESS IN LONDON

The first visit to England by the International Federation of Associations of Textile Chemists and Colourists will be made in 1959 when the *host member Society* will be The Society of Dyers and Colourists

The Congress will be held on
WEDNESDAY THURSDAY FRIDAY 16 17 18 SEPTEMBER 1959
with the Congress centre at

CHURCH HOUSE, DEAN'S YARD, WESTMINSTER, LONDON
where international language translations will be available by speech amplification and simultaneous interpretation ear-phone equipment connected to all seats

Headquarters Hotel — GROSVENOR HOUSE, PARK LANE, LONDON
Telephone Grosvenor 6363   *Telegrams* AUDLEY LONDON

During the Congress the social events will include a Dinner and Gala Ball in
The Great Room, Grosvenor House, Park Lane, London
on
Friday evening 18 September 1959
The social events will also include tours and special attractions for the ladies

Already heavy advance reservations have been received for tickets and all interested are invited to communicate with —

THE GENERAL SECRETARY
THE SOCIETY OF DYERS AND COLOURISTS
DEAN HOUSE · 19 PICCADILLY · BRADFORD 1 · YORKSHIRE · ENGLAND

A

The Journal of the Society of Dyers and Colourists

NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–7 of the January 1958 and pages 285–290 of the July 1957 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

. . . and inwardly digest	*S. Burgess*
Some Aspects of Bleaching with Hydrogen Peroxide and with Peracetic Acid	*L. Chesner and G. C. Woodford*
The Dyeing of Fast-to-washing Colours on Wool Yarn	*J. F. Gaunt*
The Work of a Colourist in a Dyehouse Laboratory	*J. T. Lynes*
The Manufacture of Coated Fabrics	
The Processes used and their Bearing on the Choice of Pigments	*H. Shepherd*

COMMUNICATIONS

The Dyeing of Secondary Cellulose Acetate with Disperse Dyes	
VII— A Comparison with their Solubility in Organic Solvents	*C. L. Bird*
Studies in the Transfer of Disperse Dyes to Cellulose Acetate during Steaming	*E. H. Daruwalla and V. R. Limaye*
The Latest Trends in the Development of the Field of Azoic Dyes	*M. Hückel*
Organo-tin Compounds as Textile Preservatives	*H. J. Hueck and J. G. A. Luijten*

EXPLANATORY PAPER ON MODERN THEORY

Surface Activity, Solution, and Adsorption	*C. H. Giles*

Solar 3 L

Substantive dyestuffs
with outstanding fastness
to light in pale
shades. Very suitable for
crease resist processing.

Solar Yellow
3 LG p.a.f.

* A pure greenish yellow
  with outstanding
  levelling properties and
  very good wet fastness.

* Suitable for after
  treatment with
  Sandofix WE, Cuprofix
  SL or Resofix CU.

* No depreciation of
  light fastness in
  combination shades.

* Excellent acetate
  rayon reserve.

Solar Discharge
Orange 3 LG

* A yellowish orange.
  Very good neutral
  and alkaline discharge
  properties.

* Excellent acetate
  reserve.

* No depreciation of
  light fastness in
  combination shades.

* Suitable for application
  for padding.

* Protected by patent rights
  in many industrial countries.

SANDOZ PRODUCTS LTD   BRADFORD

Proceedings of the Society

THE FIFTH LONDON LECTURE

The Art of Costume

ANNE M. BUCK

*Meeting of the London Section held at the Waldorf Hotel, Aldwych, on 11th October 1957,
Dr. T. H. Morton in the chair*

A well illustrated account of the trends of European fashion in clothes during the past few centuries is summarised.

The art of costume began when shears first played over the work of the loom; when the woven fabric which had for a long time been an end and a satisfaction in itself became in its turn the raw material for a new achievement, and to cut into it was no longer destruction but the first step to a new creation.

The draped length of fabric became a garment, shaped to the human body, and this relationship, the limitation imposed by the small structure and comparatively unvarying form of the human body, is the constant underlying pattern in the art of costume. Yet bound by this limitation as it has been, it has shown through many centuries an amazing richness and variety, which are not haphazard.

A slowly evolving pattern, visible only over the styles of many generations, but repeated several times in the history of costume since the Middle Ages, is the movement of dress from a loosely draped garment to one which fits the body and reveals it more closely, then to one which emphasises or exaggerates one or another part of it, and finally to a stiffened shape imposed on the body as dress reaches its point of greatest divergence from the human form (*illustrated by many lantern slides*).

Because the change is gradual, each style evolving from the one before, the body adjusts itself to these changing forms and accepts the subtle transformations given to it by succeeding expressions of the art of costume. The transforming power of dress is so great that, dominated by the form of our own time, we are almost deceived into believing that earlier styles were worn by bodies in some way different from our own. This is the real achievement of the art of costume.

The line of fashion, of any period, is shared with other arts of the time, and each generation of dress shows a penetration of decorative details, which link it with the other decorative arts of the time.

Although for the last hundred years or more the art of costume has been less apparent in the dress of men, bound by the limits of certain forms and fabrics and subdued to a narrow range of colour, it previously shared these cycles and patterns. It shows the same dominance of the line of style over the line of the body. Men often look rather disbelievingly, and a little pityingly, at the sloping shoulders of the eighteenth-century suits shown at Platt Hall: but they square themselves comfortably into shoulders provided for them by their tailors.

The fabrics which embody the changing styles, in their textures and colours, make another pattern within the art of costume. In one of the major changes of costume, the change of style in the dress of men at the end of the eighteenth century, it is the change in fabric and colour, not in line, which stays as a lasting influence in men's dress, giving it a new resistance to the art of costume itself.

The fabric of the formal and fashionable wear of men in the eighteenth century had been silk, rich in weave and colour and often flowered over with embroidery. But woollen cloth was the wear for undress and for country life. This, penetrating into men's dress, had by the beginning of the

nineteenth century taken complete possession of it, and gradually colour left it for black and dark blue, until a uniformity of texture and a limitation of colour stilled the movement of fashion there in the nineteenth century.

In women's dress the eighteenth-century style was composed in stiff, heavy silk, varied in colour and colour combinations. Then light silks replaced the heavier brocades, the woven patterns became smaller, more scattered, and delicate, finally breaking up into tiny sprigs, scaled down to the smaller area of the dress. Cotton and muslin, first in morning and undress wear, entered formal and fashionable dress. Colour was used more sparingly and grew lighter in tone, until by the last years of the century the dominance of white muslin was complete, and was to last for a quarter of a century.

In the collection at Manchester there are about seventy dresses belonging to the years 1800–1820. Of these more than half are entirely white, and of the remainder another third have a white ground with only a light sprinkling of colour in a woven, printed, or embroidered pattern. Colour— a single, clear, pale colour— appeared in the accessories— in hat, gloves, shoes, or scarf— but there was always the background of white. No dress other than a white one was worn with a coloured spencer or pelisse.

As the plain lines of the dress became more and more decorated, colour began to deepen. The colouring depended on movement, under light falling from many small sources; on the shifting colour given by the lustre of a coloured satin slip beneath an overdress of almost transparent net or gauze, or white satin beneath thin crêpe, pale pink, blue, or yellow; the contrast of the delicate gauze with the satin ornament applied in intricate patterns over bodice and hem. Colour was returning not only in the more general wearing of coloured silks and the deepening colours in them, but in the printed muslins. The dresses of the late 1820s and 1830s show many examples of beautifully printed muslins and chintzes in naturalistic patterns, but there are also interesting examples of abstract designs, and the printed patterns appear not only on cotton but also on wool and silk.

During the 1830s, as colour reached a climax of brightness and freedom, black appeared as a background to it, particularly in the cashmere shawls with vivid woven borders and satin shawls embroidered in coloured silks, in black accessories, and in black silk lace as trimming. The combination of black with colour remained in the 1840s, when the defined patterns of the 1830s had merged into more subtle shadings, in black lace flounces which covered the full skirts of evening dresses, black veiling pink, blue, green, or gold. The merging of colour into colour was expressed in shot silks, plain or figured, a silk made and much worn as early as the sixteenth century, when "changeable taffeta" was often found, not only in entries in accounts and inventories, but as part of the vivid imagery of the age. Shakespeare finds in it the image of the changeable mind, in *Twelfth Night*: "And the tailor make thy doublet of changeable

taffeta for thy mind is a very opal". The changeable silks of the 1840s were usually opalescent in pale pink, blue, green.

In the 1850s more defined patterns returned in silks, which were striped and checked, and particularly characteristic of this decade were the flounces woven with their own striped patterns, which made horizontal lines across the wide skirt. These flounces *à disposition* were found in woven and printed materials and in floral as well as striped patterns.

A taste for stronger, deeper colour actually preceded the technical achievements of 1856, which added new colours to fashion. The new colours sometimes appeared in unexpected places—

> Magenta is the favourite shade for coloured petticoats this winter . . . stockings made in the same colour are also universally worn, either plain or striped with black [1].

Scarlet also flashed through the 1860s, but as it was a colour usually given to the fine woollen fabrics this too appeared, or was concealed, in underwear, and in outer garments, in the wraps and mantles of evening wear, almost always with black, white, or black and white. But amongst the new colours the one which is most evocative of the 1860s is its bright blue, worn constantly throughout the decade.

During the 1880s there was a new infusion of the warmer reds, browns, and yellows, and more startling combinations of colour— bronze and blue, olive green and pink, garnet and myrtle. There was at the same time a fashion for combining two textures in the same colour— plush, a material very popular for those years, with satin, or satin with cashmere; and also the combining of a plain with a figured fabric. The names given to the fashionable colours were redolent of good living— claret, chartreuse, salmon, prawn, chestnut, cigar, amber, garnet, ruby.

During the 1890s crimson, purple, and yellow were particularly fashionable, but then fabric and colour once again became lighter and softer. Warp-printed fabrics are very characteristic of the years 1900–1910, and their effect of shifting colour and blurred pattern helped to make the character and the quality of early twentieth-century dress.

All the elements that go to make up the art of costume, the relation of fabric to form and colour, texture and ornament to fabric, never combine in exactly the same way. All are subject to the intangible influences which are crystallised in the decorative arts of an age, amongst which the art of costume takes its place. And although the works of this minor art survive only imperfectly outside their own time, separated from the living forms which wore them, yet each carries within it still the qualities which are of its own moment of time and no other.

GALLERY OF ENGLISH COSTUME
    MANCHESTER CITY ART GALLERIES

Reference

[1] *Englishwoman's Domestic Magazine* (Dec. 1860).

Symposium on "Recent Advances in the Colouring of Man-made Fibres"

The Flash-ageing of Vat-printed Viscose Rayon Fabrics

A. S. FERN and W. F. LIQUORICE

The evolution of pad–steam processes for fixing printed vat dyes on cellulosic fabrics is traced. The behaviour of a wide range of vat dyes under laboratory "flash-ageing" conditions with sodium dithionite (hydrosulphite)–caustic soda as the reducing system indicated the most satisfactory thickening agent, dyes, and padding and steaming conditions, and led to the design of a bulk-scale steamer operating at about 7 yd./min. with a steaming time of about 20 sec. The percentage fixation of a selected range of dyes on viscose rayon and on cotton under flash-ageing conditions compares favourably with that obtained by the "all-in" sulphoxylate–carbonate printing process, where the steaming time is sixty times as long. Many vat dyes show improved brightness and/or colour value when steamed for short times, owing to the absence of leuco decomposition or over-reduction. Such a flash-ageing process is ideally suited to screen printers and to those machine printers of all-vat styles who wish to augment their steaming capacity with little capital expenditure. A modified process is being worked out with thiourea dioxide as reducing agent in the printing paste, development being by padding with caustic soda before steaming. This is particularly suitable for designs of low coverage, or where it is essential to process other types of dyes alongside vat dyes. Preliminary experiments indicate that emulsion thickenings are unlikely to show much technological advantage over conventional thickenings in the flash-ageing process.

I— Introduction

Many methods of applying vat dyes to fabrics have been devised, all depending at some stage on reducing the insoluble quinone form to the water-soluble leuco form and then oxidising back to the quinone on the fibre. The necessity for the reduction stage coupled with the individual properties of the commercially available vat dyes and the varied requirements of the textile trade has given rise to a complicated technology. For dyeing, sodium dithionite (hydrosulphite) (C.I. Reducing Agent 1) in caustic alkaline solution is a reducing system sufficiently powerful for the reduction of all vat dyes. In textile printing, however, where the fabric is normally dried before steaming, sodium hydrosulphite cannot be used in the print paste, and a more stable reducing agent, viz. sodium formaldehyde-sulphoxylate (C.I. Reducing Agent 2), has become generally accepted, in conjunction with sodium or potassium carbonate (the "all-in" vat printing process). This is a weaker reducing system than hydrosulphite and caustic soda, and is not capable of reducing all vat dyes; the range suitable for printing by the all-in method is therefore limited. Furthermore, although sulphoxylate is relatively stable, it does decompose on exposure of the print to air between printing and steaming[1], and often gives irregular results, especially under screen-printing conditions. These difficulties were overcome by the "pad–steam" printing method, first published in 1926 (although there is convincing evidence that it was in use as early as 1911 in France[2]), and now well known as the *Colloresin* or *locust-bean gum* method, in which the print paste contains only dye and a thickening capable of coagulation by alkali, reduction being brought about by padding with an alkaline reducing agent and steaming. Sulphoxylate and alkali-metal carbonate were first recommended[3] as the reducing medium with a steaming time of 5 min., but since the padded print need not be

dried before steaming, hydrosulphite and caustic soda were later recommended[4], and the steaming time was reduced to 30 sec. by using a "rotary chest".

Although an increased range of dyes was applicable by the latter method, it did not become popular, and the sulphoxylate method with a steaming time of several minutes became established; it is still widely used in the United Kingdom and in some European countries, often being associated with high-quality cotton and linen furnishing prints. The obvious technical advantages of this type of process are— (a) the possibility of storing the printed fabric indefinitely before steaming, (b) the use of certain vat dyes of high light fastness which are difficult to print by the all-in method using sulphoxylate, and (c) freedom from difficulties where the prevailing conditions cause a loss of sulphoxylate in the printed areas. Some of the fundamental problems inherent in all-in printing with vat dyes have been discussed by Thornton and Liquorice[1] and by Michie and Thornton[5].

Developments in the pad–steam vat dyeing process during the 1939–1945 war probably contributed to the fresh appraisal of the corresponding printing process instituted by E. I. du Pont de Nemours & Co. Inc. and led to the publication of certain novel features[6, 7]. The alkali-coagulable thickening was considered unnecessary, the printed mark being maintained by applying the hydrosulphite and caustic soda from a thickened solution by means of an engraved roller or screen (hence the alternative name *blotch-printing*). A similar variation of the Colloresin process, using sulphoxylate and sodium carbonate applied from a stipple roller, had previously been described by Diserens[8]. The process has not met with widespread success in the U.S.A., although several firms in Japan are believed to be operating it successfully. Some modifications have recently

been proposed [9], based on the use of water-in-oil emulsion thickenings and special vat dyes (the Vantasol (DuP) range). In this Savagraph process, the reducing solution is again applied to the cloth by a pad mangle instead of from a thickened print paste. Some comments on the use of emulsion thickenings in the flash-ageing process are given later in this paper.

Emphasis has been laid throughout on the processing of viscose rayon fabrics, since the sulphoxylate pad–steam process has never been widely applied to these, but most of the technical information applies equally to cellulose in other forms.

II— Description of the Process

In this paper the term *flash-ageing* refers to a process comprising the following stages—

(1) The vat dye is dispersed in a thickening agent capable of coagulation by alkali, printed, and dried. There is no need to proceed immediately to Stage (2)

(2) The fabric is padded in a slightly thickened solution of sodium hydrosulphite and caustic soda

(3) Immediately after Stage (2) the fabric is steamed in saturated air-free steam at about 100–102°c. for 15–30 sec.

(4) Immediately after Stage (3) the fabric is oxidised and soaped in the normal manner for vat dyeings.

This process offers a number of attractions to both screen and machine printers, e.g.—

(a) The complete stability of the prints between printing and steaming avoids irregular yields due to decomposition of reducing agent. Any goods incorrectly printed can readily be freed from print paste

(b) Brighter colours result from the very short steaming times because of the absence of dye decomposition, which is unavoidable with many dyes when steamed for 5–20 min.

(c) Some dyes possessing desirable fastness properties or colour, and not applicable with sulphoxylate as the reducing agent, can be used

(d) The comparative simplicity of the steamer with the consequent lower capital cost of installation and maintenance

(e) The small-volume steamer offers a considerable saving of steam

(f) The small yardage of cloth in process at a particular time results in small losses in case of accidental stoppage, etc.

(g) Faults in printing, padding, steaming, or soaping are quickly detected and eliminated.

It is generally claimed that the use of hydrosulphite and caustic soda permits the use of a wider range of dyes than is applicable with sulphoxylate and alkali-metal carbonate. From the point of view of ease of reduction this is true, but the advantage is partly offset by the fact that some of the dyes which require hydrosulphite for reduction have low affinities and give rise to flushing, i.e. lateral migration of dye leading to loss of definition. The recommended range is still adequate and includes a number of dyes

having attractive colour and fastness properties which are not applicable by conventional methods, as well as many well established printing vat dyes.

The flash-ageing process is applicable to all cellulosic fibres, and to Ardil–viscose rayon blends. Satisfactory semi-bulk-scale runs of up to 500 yd. have been carried out with mercerised and unmercerised cotton, spun viscose rayon of light and heavy construction, and bleached and unbleached linen. The only variations of the process required for different fabrics are mechanical modifications at the padding stage to ensure complete wetting-out of the heavier fabrics.

III— Experimental

A. MATERIALS AND TECHNIQUE

VISCOSE RAYON STAPLE FABRIC— 18s singles, 10 t.p.in. Z twist; picks 62, ends 89, wt. 3·6 oz. per sq.yd.

DYES— Commercially available paste and powder brands.

CHEMICALS— Commercial qualities.

F	Face side of print
I	Pyrex glass tube, 36 in. × 3 in.
2	Brass end-pieces
3	Rubber washers
4	Springs securing end-pieces
5	Guide-rollers
6	Lips to keep mouthpiece dry
7	Outlet for condensate
8	Iron tube filled with copper turnings
9	Electrical heating element
10	Insulation (slot provided for viewing inside steamer)
11	Thermometer
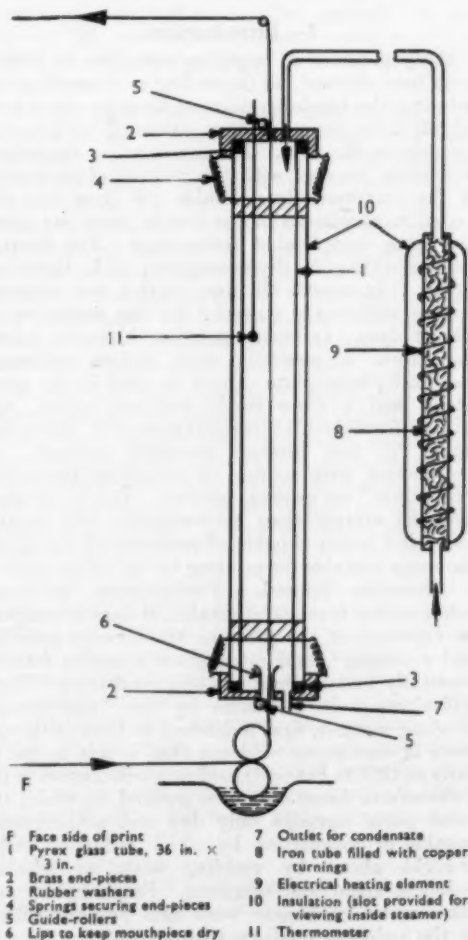
FIG. 1— Laboratory-scale Flash-ager

THICKENING AGENTS—

Gum Gatto— Ellis Jones Ltd., Stockport

Manutex RS— Alginate Industries Ltd., London

Meypro Gum PLU— Meypro Ltd., Weinfelden, Switzerland

Cellofas A— ICI

Indalca U— Cesalpina, Milan, Italy

Nafka Crystal Gum— W. A. Scholten's Chemische Fabrieken NV., Groningen, Holland.

The percentage fixation of a vat dye was estimated colorimetrically by the method described by Michie and Thornton[5].

LABORATORY-SCALE STEAMER— For experimental work and for the pitching of shades in the laboratory, the small-scale steamer shown in Fig. 1 was used. It consists essentially of a Pyrex glass tube of 3 in. diameter and 36 in. long, with brass end-pieces in which are cut slots as mouthpieces. The print is padded by means of a power-driven domestic washing-machine mangle fitted with a small stainless-steel padding trough. The speed of the mangle is adjusted to give the required steaming time. Owing to the short length of the steamer, the running speed is slow, and it is essential that the padding nip be within a few inches of the mouthpiece.

B. THE DYE

The chief factors which would be expected to affect the suitability of a vat dye for flash-ageing are—

(1) The extent to which the reducing system is capable of converting the dye to its leuco form

(2) The rate of reduction

(3) The affinity of the leuco dye for the fibre

(4) The physical properties of the vat dye preparation as marketed.

(1) Extent of Reduction

It is known empirically that a hydrosulphite–caustic soda system will completely reduce all commercially available vat dyes, usually at temperatures well below 100°c. Marshall and Peters[10] investigated the reduction of many vat dyes and concluded that the extent to which they could be reduced was best expressed by their "leuco potential". The vat dyes they examined covered a range of leuco potentials from about −750 mv. to about −1000 mv., those dyes with the highest negative potentials being most difficult to reduce. Since the reduction potential of hydrosulphite–caustic soda is about −1140 mv. at 60°c., it is readily deduced that such a system should effectively reduce the range of vat dyes. (The reduction potential of a normal British gum–sulphoxylate–potassium carbonate print paste is about −960 mv. Hence the difficulty of achieving maximum colour value from certain vat dyes with this system.)

It is concluded that the reducing system used in flash-ageing is potentially capable of converting *all* vat dyes completely to the leuco form.

(2) Rate of Reduction

When a print is to be fixed by steaming for 30 sec. or less, it would be thought that the rate of reduction would be a limiting factor, since only leuco dye can be adsorbed by the fibre. A low reduction rate could also contribute to flushing during steaming, since unreduced dye would bleed out from the printed areas more readily than a leuco dye having affinity for cellulose. Sumner (private communication) measured the rates of reduction of 71 vat dyes in a solution of 2% caustic soda and 2% sodium hydrosulphite at 50°c., and converted them to the values at 100°c. by means of the relationship between rate of reduction and temperature found by Marshall and Peters[11]. Table I shows the times in seconds for 95% reduction for the dyes tested. The concentrations of caustic soda and hydrosulphite used in flash-ageing are generally higher than those used in the above determinations, so that in practice the reduction times should be even shorter. The time required for the reduction of the majority of vat dyes is thus within the range required for flash-ageing.

TABLE I

Time for 95% Reduction (sec.)	No. of Dyes reduced (converted to 100°c.)
0–5	31
5–10	15
10–15	10
15–20	8
Over 20	7

To test the efficiency of the flash-ageing process, some preliminary experiments were made in which a large number of vat dyes were printed and then steamed for 8 sec. and 40 sec., and the percentage fixation was compared with that obtained by the normal sulphoxylate–carbonate method, steamed for 8 min. The results indicated that the ultimate percentage fixation obtained by flash-ageing is generally higher than that produced by the conventional method. Although fixation is not complete within 8 sec., it has in many cases reached a stage at which the greater yield obtained by prolonging the steaming to 40 sec. may be offset by the lower production rate and the increased risk of flushing. A more detailed examination of a smaller number of vat dyes showed that many dyes reached maximum fixation in approx. 20 sec., and that careful selection could give a range suitable for development in even shorter times. (See Table II.)

It should not be thought, however, that the rate of reduction is entirely unimportant in selecting suitable dyes for flash-ageing. A comparison of Durindone Printing Pink FF 125 paste (normal reduction rate) with QF Durindone Printing Pink FF Paste (special form having high reduction rate) shows that the latter is suitable, and the former unsuitable, for this method of application.

TABLE II

Fixation of Vat Dyes recommended for Application by Flash-ageing

Dye	Colour Index No.	Printing Strength (%)	Viscose Rayon			Cotton			Sulphoxylate "All-in" Cotton
Time of steaming		...	8 sec.	20 sec.	40 sec.	8 sec.	20 sec.	40 sec.	8 min.
Caledon Printing Yellow 6GS Paste	C.I. Vat Yellow 27	13	81	83	81	64	63	72	74
Caledon Printing Yellow 5GK 150 Paste	C.I. Vat Yellow 26	7·5	92	88	87	77	81	80	75
Caledon Printing Yellow 5GS Paste	C.I. Vat Yellow 2	12	84	94	91	77	88	87	56
Caledon Printing Yellow GNS Paste	C.I. Vat Yellow 1	14	97	97	84	91	92	92	83
Caledon Printing Orange GS Paste	C.I. Vat Orange 9	18	80	90	88	75	84	88	65
Caledon Gold Orange 3G 200 Paste Fine	C.I. Vat Orange 15	7	88	99	97	77	82	87	52
Caledon Printing Orange 2RTS Paste	C.I. Vat Orange 2	21	88	88	89	84	88	88	84
Caledon Printing Orange 4RNS Paste	C.I. Vat Orange 4	22	87	88	89	84	88	94	72
Caledon Printing Orange 6RS Paste	C.I. Vat Orange 3	13	85	86	91	76	80	81	70
Caledon Printing Red 3B 200 Paste	C.I. Vat Red 10	10	86	91	94	77	81	86	52
Caledon Red 2GN 150 Paste Fine	C.I. Vat Red 23	12	91	93	93	77	78	79	37
QF Caledon Printing Scarlet G Paste	C.I. Vat Red 37	15	81	86	85	79	77	78	73
FD Caledon Rubine B Powder Fine	—	4	88	88	95	76	83	85	63
QF Durindone Printing Pink FF Paste	C.I. Vat Red 1	10	80	84	95	82	90	95	80
QF Durindone Printing Red 3B Paste	C.I. Vat Violet 2	9	58	71	81	52	67	72	72
Caledon Printing Purple 4RS Paste	C.I. Vat Violet 1	—	Unsuitable for optical estimation						
Caledon Brilliant Violet 3BS Paste Fine	C.I. Vat Violet 9	15	81	91	93	81	89	93	60
Caledon Violet XBNS Paste Fine	C.I. Vat Violet 13	15	97	99	98	93	97	97	78
QF Durindone Printing Magenta B Paste	C.I. Vat Violet 3	10	82	90	94	84	86	90	72
Caledon Printing Blue XRNS Paste	C.I. Vat Blue 4	15	74	90	82	71	77	82	49
Caledon Printing Blue GCPS Paste	C.I. Vat Blue 14	15	90	92	90	85	87	85	49
Caledon Printing Blue 3GS Paste	C.I. Vat Blue 12	16	88	90	92	87	83	86	60
Caledon Blue XRCS Paste Fine	C.I. Vat Blue 6	20	62	71	71	69	75	74	24
FD Caledon Blue 3RC Powder Fine	—	3	88	93	90	86	86	89	35
Caledon Printing Navy GS Paste	C.I. Vat Blue 16	10	84	96	95	91	95	97	84
Caledon Printing Dark Blue 2RS	C.I. Vat Blue 17	11	87	91	93	80	84	92	78
Caledon Printing Jade Green XBNS Paste	C.I. Vat Green 1	14	88	92	92	80	93	92	83
Caledon Printing Jade Green 2G 300 Paste	C.I. Vat Green 2	12	91	97	95	81	85	84	78
Caledon Printing Green 6BS Paste	C.I. Vat Blue 7	9	86	92	90	90	93	91	78
Caledon Green 7G 200 Paste Fine	C.I. Vat Green 16	9	88	94	93	79	84	88	68
Caledon Printing Olive Green BS Paste	C.I. Vat Green 3	10	91	94	98	87	92	95	62
Caledon Printing Brown 4RS Paste	C.I. Vat Brown 28	7	85	88	87	77	82	82	66
Durindone Printing Brown GS Paste	C.I. Vat Brown 5	10	84	92	91	71	75	80	70
Caledon Printing Grey BS Paste	C.I. Vat Black 24	10	93	94	92	91	92	97	80
QF Caledon Printing Black 2R Paste	—		Unsuitable for optical estimation						
QF Durindone Printing Black BL Paste	C.I. Vat Black 1	15	61	81	86	73	81	80	71
QF Durindone Printing Black TL Paste	C.I. Vat Black 1	15	81	90	91	75	80	86	71
FD Caledon Grey M Powder Fine	C.I. Vat Black 8	5	95	93	97	84	84	86	55

TABLE III

Fixation (%) of Different Forms of C.I. Vat Red 1 on Viscose Rayon

. (printed at equal dye concentration in the print paste)

	Flash-ageing			Sulphoxylate–Carbonate
Time of steaming ...	8 sec.	20 sec.	40 sec.	8 min.
Durindone Printing Pink FF 125 Paste ...	61	73	83	63
QF Durindone Printing Pink FF Paste	85	97	97	80

(3) *Affinity for Fibre*

Leuco vat dyes vary widely in the extent to which they are absorbed by cellulose at equilibrium, and in the rate at which this absorption is attained. For flash-ageing it is clearly desirable to choose those dyes which exhaust most rapidly and completely, since dyes that are retained more completely in the aqueous phase after 20 sec. steaming not only give low tinctorial value, but also are more likely to diffuse from the printed areas.

The importance of rate of absorption of the leuco compound is illustrated by the results obtained with those dyes listed in Table IV. Although the percentage fixation of most of these dyes is high, many are considered unsuitable for flash-ageing owing to their tendency to flush during

steaming, and it would appear that the leuco compound must be almost completely absorbed in the first few seconds if a satisfactory print is to be obtained. The dyes were printed in heavy depths in stripes on unmercerised cotton fabric with the thickening described in § C, and then padded with the stripes perpendicular to the direction of padding, in order to show more clearly any loss of definition at the printed edge. Steaming was carried out for 40 sec. No thickening agent was added to the pad liquor in this case in order to provide deliberately unfavourable conditions. Dyes were chosen at random from each group, and repeat tests were carried out with viscose rayon. It was clear that the extent of flushing on the latter fabric was always less than on cotton. The classification is given in Table IV.

TABLE IV

Tendency of Dyes to Flushing

GROUP I

NO FLUSHING AND SHOULD BE SATISFACTORY ON VISCOSE RAYON AND COTTON EVEN UNDER UNFAVOURABLE CONDITIONS

Caledon Printing Yellow 5GS Paste	C.I. Vat Yellow 2
Caledon Printing Yellow GNS Paste	C.I. Vat Yellow 1
Caledon Printing Orange 4RNS Paste	C.I. Vat Orange 4
Caledon Printing Orange 6RS Paste	C.I. Vat Orange 3
Caledon Printing Orange 2RTS Paste	C.I. Vat Orange 2
Caledon Red 2GN 150 Paste Fine	C.I. Vat Red 23
Caledon Printing Blue GCPS Paste	C.I. Vat Blue 14
Caledon Blue XRCS Paste Fine	C.I. Vat Blue 6
Caledon Printing Blue 3GS Paste	C.I. Vat Blue 12
Caledon Printing Blue XRNS Paste	C.I. Vat Blue 4
Caledon Printing Olive Green BS Paste	C.I. Vat Green 3

GROUP II

SLIGHT FLUSHING UNDER ADVERSE CONDITIONS BUT SHOULD BE SATISFACTORY WITH NORMAL CARE. ON VISCOSE RAYON BEHAVE AS GROUP I DYES

Caledon Printing Yellow 6GS Paste	C.I. Vat Yellow 27
Caledon Yellow 5GK 150 Paste Fine	C.I. Vat Yellow 26
Caledon Printing Orange GS Paste	C.I. Vat Orange 9
Caledon Gold Orange 3G 200 Paste Fine	C.I. Vat Orange 15
Caledon Printing Brown 4RS Paste	C.I. Vat Brown 28
Caledon Printing Red 3B 200 Paste	C.I. Vat Red 10
Caledon Red 5GS Paste Fine	C.I. Vat Red 42
FD Caledon Rubine B Powder Fine	—
Caledon Printing Purple 4RS Paste	C.I. Vat Violet 1
Caledon Printing Violet 3BS Paste	C.I. Vat Violet 9
Caledon Violet XBNS Paste Fine	C.I. Vat Violet 13
FD Caledon Blue 3RC Powder Fine	—
Caledon Printing Navy GS Paste	C.I. Vat Blue 16
Caledon Dark Blue 2R 150 Paste Fine	C.I. Vat Blue 17
Caledon Printing Green 6BS Paste	C.I. Vat Blue 7
Caledon Green 7G 200 Paste Fine	C.I. Vat Green 16
Caledon Printing Jade Green 2G 300 Paste	C.I. Vat Green 2
Caledon Printing Jade Green XBNS Paste	C.I. Vat Green 1
FD Caledon Grey M Powder Fine	C.I. Vat Black 8
QF Caledon Printing Black 2R Paste	—
QF Durindone Printing Pink FF Paste	C.I. Vat Red 1
QF Durindone Printing Magenta B Paste	C.I. Vat Violet 3
QF Durindone Printing Red 3B Paste	C.I. Vat Violet 2
Durindone Printing Brown GS Paste	C.I. Vat Brown 5
QF Durindone Printing Black BL Paste	C.I. Vat Black 1
QF Durindone Printing Black TL Paste	C.I. Vat Black 1

GROUP III

APPRECIABLE FLUSHING. COULD BE USED ONLY UNDER FAVOURABLE CONDITIONS. ON VISCOSE RAYON BEHAVE AS GROUP II DYES

Caledon Printing Yellow GKS Paste	C.I. Vat Yellow 4
Caledon Yellow 4GS Paste Fine	C.I. Vat Yellow 13
Caledon Brown RS Paste Fine	C.I. Vat Brown 3
Caledon Dark Brown 2GS Paste Fine	C.I. Vat Brown 49
Caledon Printing Red BNS Paste	C.I. Vat Red 35
Caledon Printing Pink RLS Paste	C.I. Vat Red 43
Caledon Red X5B 200 Paste Fine	C.I. Vat Red 19
FD Caledon Brilliant Red 5B Powder Fine	—
Caledon Brilliant Violet RS Paste Fine	C.I. Vat Violet 17
Caledon Brilliant Violet 3R 200 Paste Fine	C.I. Vat Violet 12
Caledon Red Violet 2RNS Paste Fine	C.I. Vat Violet 14
FD Caledon Green 2B Powder Fine	C.I. Vat Green 11
Caledon Green RCPS Paste Fine	C.I. Vat Green 6
Caledon Printing Jade Green 3B 200 Paste Fine	C.I. Vat Green 4
Caledon Olive D Paste Fine	C.I. Vat Black 25
Durindone Printing Pink 2BS Paste	C.I. Vat Red 11
Durindone Printing Blue 4BCS Paste	C.I. Vat Blue 5

GROUP IV

MUCH FLUSHING. UNSUITABLE

Caledon Yellow 2RS Paste Fine	C.I. Vat Orange 12
FD Caledon Yellow 3R Powder Fine	—
Caledon Brown 3G 150 Paste Fine	C.I. Vat Brown 30
Caledon Dark Brown 3RS Paste Fine	C.I. Vat Brown 1
Caledon Dark Brown 6R 200 Paste Fine	C.I. Vat Brown 38
Caledon Brown B 200 Paste Fine	C.I. Vat Brown 23
Caledon Khaki 2G 150 Paste Fine	C.I. Vat Green 8
Caledon Khaki R 150 Paste Fine	C.I. Vat Brown 47
Caledon Olive R 125 Paste Fine	C.I. Vat Black 27
Durindone Printing Orange R 150 Paste	C.I. Vat Orange 5
Durindone Printing Scarlet YS Paste	C.I. Vat Red 45
Durindone Printing Red BS Paste	C.I. Vat Red 41
Indigo P 20% Paste	C.I. Vat Blue 1
Indigo 2RS Printing Paste	C.I. Vat Blue 34
Carbindone Printing Black BS Paste	—

Table V shows that there is a correlation, although not an exact one, between the thermodynamic affinity of the leuco dye on cotton as measured at 40°c. by Marshall and Peters [10], using the method of Fowler, Michie, and Vickerstaff [12], and the group in which the dye has been placed according to its tendency to flush.

Under bulk-scale conditions the tendency to flush is much less than is indicated by these laboratory trials, but, nevertheless, the classification gives a useful guide to the relative merits of individual vat dyes. This information together with the rate of fixation enabled a choice of the most suitable dyes to be made, for large-scale evaluation.

TABLE V

Dye (in order of affinity on cotton) (*highest*)	Colour Index No.	Flushing Group
Caledon Printing Purple 4R	C.I. Vat Violet 1	2
Caledon Printing Red 3B	C.I. Vat Red 10	2
Caledon Printing Yellow GN	C.I. Vat Yellow 1	1
Caledon Printing Yellow 5G	C.I. Vat Yellow 2	1
Caledon Printing Jade Green XBN	C.I. Vat Green 1	2
Caledon Brown R	C.I. Vat Brown 3	3
Durindone Printing Brown G	C.I. Vat Brown 5	2
Caledon Printing Red BN	C.I. Vat Red 35	3
Caledon Brilliant Violet R	C.I. Vat Violet 17	3
Durindone Printing Scarlet Y (*lowest*)	C.I. Vat Red 45	4

(4) Physical Form of Vat Dye

Owing to the differences in properties between individual vat dyes, and the widely varying conditions of dyeing and printing, many specially prepared brands have been produced. The chief objective in the preparation of printing qualities has hitherto been those physical properties which will lead to a rapid rate of fixation and freedom from speckiness with the conventional sulph-oxylate–carbonate process. In many cases this has resulted in the introduction of reduction catalysts. Under flash-ageing conditions, however, with the more powerful hydrosulphite–caustic soda system, reduction is very rapid, and the advantages given by reduction catalysts are less apparent. In some cases, therefore, dyeing brands, such as the finely dispersed FD Caledon Powders Fine, are as suitable for flash-ageing as are the printing pastes. This is not always true, however, and in cases where the rate of reduction is exceptionally low, e.g. with certain thioindigoid-type dyes, the rapidly reducing printing qualities are essential for flash-ageing.

The non-drying agents present in some printing pastes tend to slow down the rate of fixation and thus promote flushing. The extent of the effect depends on the molecular weight of the hygroscopic agent. Thus, agents of low molecular weight, e.g. glycerol or ethylene glycol, have very little adverse effect, whereas with glycols of higher molecular weight, e.g. di-, tri-, or poly-ethylene glycols, the leuco vat dye is held preferentially in the aqueous phase. The suitability of a particular non-drying paste brand must, therefore, be tested under the fixation conditions encountered in practice.

C. THICKENING AGENTS FOR THE PRINT

The choice of thickening depends on the conditions of padding and the type of cloth but must always enable the printed fabric to be handled without difficulty both after printing and drying, and during padding, steaming, and wet-processing. A thickening which aggregates on entering the pad-liquor is essential if sharp definition is to be maintained, and marking-off on the pad-mangle and staining of the pad-liquor are to be avoided. At the same time the thickening should be sufficiently permeable to ensure rapid wetting out. These conditions are not related directly to the solids content of the thickening but depend on the constitution of the agent used.

Table VI shows the percentage fixation of prints of Caledon Printing Jade Green XBNS Paste printed with thickenings of various total solids content and steamed for 8 sec. and 5 min.

TABLE VI

Effect of Thickening on Fixation of Dye

(6% Caledon Printing Jade Green XBNS Paste: C.I. Vat Green 1)

Thickening	Solids Content in Print Paste due to Thickening (%)	Fixation (%)	
		Steamed 8 sec.	Steamed 5 min.
Nafka Crystal Gum...	12·6	81	88
Indalca U	7·7	87	95
Wheat starch ...	6·5	81	95
Cellofas A	6·2	50	61
Meypro gum PLU ...	4·2	85	93
Manutex RS ...	2·8	90	90
Gum Gatto	1·4	86	94
Emulsion ... ... (oil-in-water type)	1·2	82	90

A compound thickening combining a number of printing properties has been found most satisfactory. Locust-bean gum (gum Gatto) is cheap, aggregates with alkali, and ensures good definition, but when it is used alone it gives poor visual colour value; this can be improved by the inclusion of wheat starch. The gum Gatto–starch mixture gives good colour value and is suitable for printing fine lines and small pegs but on account of its high anomalous viscosity gives unlevel blotches. Modification of the flow properties by the inclusion of sodium alginate gives an economical thickening of very good general properties.

The following recipe is recommended as a guide—

25 g.	...	Wheat starch is mixed with
900 c.c.	...	Cold water, and to this is added with stirring a mixture of
10 g.	...	Gum Gatto and
10 g.	...	Alcohol

		The mixture is boiled for 15 min. and cooled, and to it are added—
2 g.	...	Sodium hexametaphosphate dissolved in
45 c.c.	...	Water, and finally
8 g.	...	Sodium alginate (Manutex RS) is added slowly with stirring

1,000 g.

If preferred, the alginate and the sodium hexametaphosphate may be prepared as a separate thickening and mixed with the gum Gatto–starch

thickening as required. When alginate is used, sodium hexametaphosphate is necessary for the production of level prints.

If it is necessary to store this thickening for prolonged periods a preservative will be required: sodium trichlorophenoxide is recommended, and formaldehyde should *not* be used.

The inclusion of borax with gum Gatto, which is sometimes used in the sulphoxylate pad–steam process to obtain improved definition, is of limited value for flash-ageing, since it produces an aggregate which tends to be too impermeable to allow penetration of the liquor through the thickening in the short steaming times used. Wetting agents are not recommended in the print paste or in the pad liquor, since they promote flushing in the steamer. In the printing of very fine fabrics, for which a more firmly aggregated thickening is desirable to minimise flushing, the proportion of gum Gatto should be increased at the expense of starch. No difficulties have been experienced with the removal of this starch-based thickening from viscose rayon, possibly because appreciable "fixation" of the starch does not take place in 20 sec. steaming.

A number of cold-dissolving thickenings are marketed in the U.S.A. specifically for flash-ageing. Some of these were tested, but none gave the same sharpness of definition as the compound thickening described above, and they tended to mark off on the pad-mangle.

D. EMULSION THICKENINGS

Reference has already been made to the possibility of replacing a conventional thickening agent by a water-in-oil emulsion containing a relatively small proportion of a polymeric binder. Experiments were carried out to assess the potential value of this approach, using the following general recipe—

5 g.	...	Paralac 64DX (ICI) is diluted with
25 c.c.	...	White spirit. To the solution is added
70 c.c.	...	Water slowly, with high-speed stirring

To the emulsion thickening so formed is added the appropriate quantity of vat-dye printing paste, again with high-speed stirring. Smooth stable pastes are obtained from many Caledon and Durindone printing pastes by this method. As is usual with emulsion thickenings, these pastes possess poor flow properties under machine-printing conditions, and readily give mottled prints from deep engravings and in large blotches under screen-printing conditions. The emulsion breaks immediately it strikes the cloth, but the vat dye does not tend to migrate at this stage, although the definition is usually inferior to that obtained with a normal thickening. When the print is dried, very little binding agent is present, and this may be insufficient to prevent the vat dye from rubbing off when the cloth is handled before steaming, thus causing coloured specks on the white portions. More dyes flush when an emulsion thickening is used, owing to the small proportion of binding

agent; flushing is aggravated still more if the binding agent is decomposed by the hot alkaline conditions experienced during steaming. Even with high-affinity dyes, the definition of the final print is often worse when an emulsion thickening is used. Difficulties such as mottled prints, poor definition, and flushing could be overcome in machine printing by using shallow engravings and by crushing, but the depth of colour obtainable would then be limited.

Under comparable fixation conditions, the penetration of prints obtained with emulsions of this type usually tends to be slightly greater than with the conventional thickening agents; this inevitably results in the colour value of the print being slightly lower.

It is considered from these preliminary experiments that there is no great technical advantage to be gained by using emulsion thickenings in the flash-ageing process, and there may be certain disadvantages.

E. THE PAD-MANGLE AND THE PADDING SOLUTION

The most suitable padding method depends largely on the type of fabric and the style of print being processed. For fine fabrics and most machine prints a nip pad is satisfactory, but for cloths of heavy construction and screen prints, particularly in blotch patterns, immersion in the padding liquor gives complete wetting-out and more even development. Bleeding-out of the vat pigment does not occur at this stage if thickening capable of coagulation by alkali has been used. For immersion in the liquor a two-bowl mangle is suitable with the cloth passing with the face side outwards round an immersed guide roller, the lower bowl of the mangle also running in the liquor (Fig. 2).
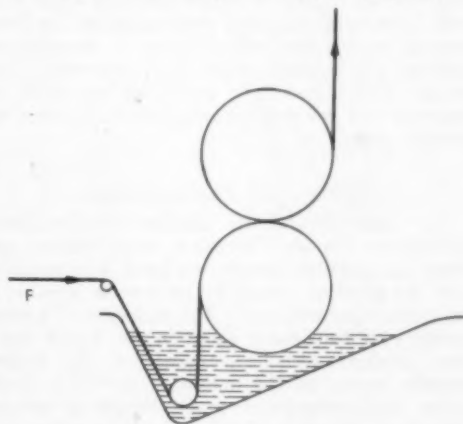
F Face side of print

FIG. 2— Recommended Method of Padding

Alternatively, the padding trough may be separated from the mangle as in Fig. 3. In this case the vertical passage from the liquor to the mangle should be short to minimise the decomposition of sodium hydrosulphite on exposure to air. Also, in this method of padding there is a risk of

F Face side of print
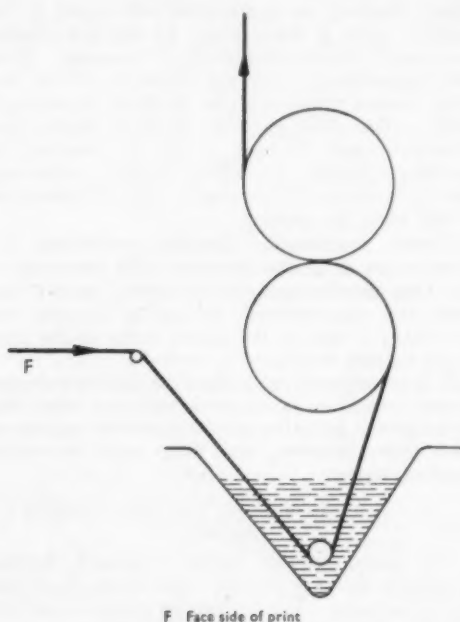
FIG. 3— Alternative Method of Padding

staining of the whites by the running down of colour loosened by the mangle. These faults are avoided by immersion of the bottom roller, which is then continuously washed with fresh pad liquor.

For consistent running, the padding trough should be of small volume and it should be fed continuously at several points along its width with fresh liquor. Continuous replenishment by fresh solution avoids the accumulation of decomposed sodium hydrosulphite, especially at the ends of the trough, and also avoids soiling of the bath by traces of vat dye removed mechanically from the printed areas.

Stability of the Padding Solution

The stability of an alkaline hydrosulphite solution on exposure to air is very limited, and when low running speeds are used it is essential that the padding mangle be as close as possible to the steamer mouthpiece. The inclusion of a small quantity of thickening agent in the liquor has a very marked stabilising effect on the hydrosulphite owing to the decreased mobility of the liquor and consequent protection from aerobic oxidation. Suitable additions for this purpose are 1% (by volume of the pad-liquor) of wheat starch or gum tragacanth added as previously prepared 5% solutions. Cold-dissolving thickenings, e.g. Indalca U or Solvitose C 5, can also be used, The addition of chemical stabilisers, e.g. formaldehyde, is not recommended, since the hydrosulphite is rendered insufficiently reactive. Fig. 4 shows the rate of oxidation of sodium hydrosulphite in caustic soda solution on exposure to air when padded on to

an unmercerised cotton fabric, and the stabilising effect of various thickening agents. The estimations were carried out by padding, exposing to air, immersing the exposed fabric in a solution of iodine, and back-titrating the excess of iodine with sodium thiosulphate. Clearly, where long runs are envisaged, steps must be taken to ensure that pad-liquor is not stored for long periods before use.

The addition of a thickening agent to the pad-liquor not only has a stabilising action on the sodium hydrosulphite but also aids furnishing on the padding rollers and is an additional safeguard in preventing flushing during steaming.

Concentration of Padding Bath

The concentrations of alkali and hydrosulphite are very important. The concentration of hydrosulphite should not fall significantly below 5% (by weight); otherwise, those vat dyes with a large negative leuco potential will be incompletely reduced. The caustic soda concentration affects both the rate of reduction of the dye and also the rate of dyeing of the fibre. A high concentration, over 5%, gives rapid reduction but slows down the rate of adsorption of the leuco dye and promotes flushing. The sharpness of definition is considerably improved by decreasing the caustic soda concentration, but on account of the acidic nature of the decomposition products of hydrosulphite the total alkali concentration should be maintained at approximately the same value as the concentration of hydrosulphite. Replacement of some of the caustic soda by sodium or potassium carbonate gives good results.
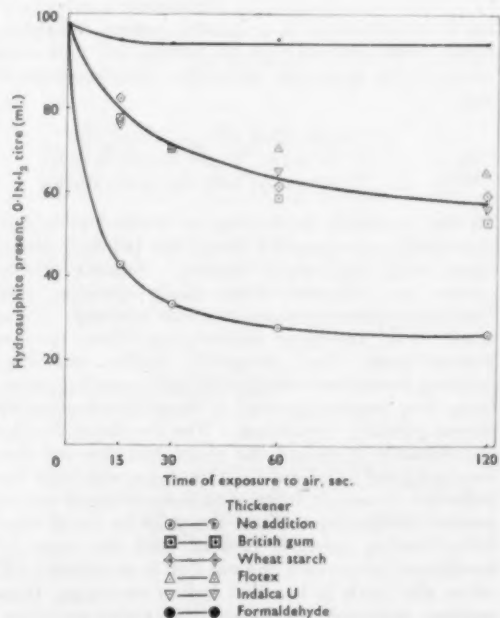
FIG. 4— Stability of Pad Liquor containing 5% Caustic Soda Flake, 5% Sodium Hydrosulphite, and Various Thickening Agents— Padded Cloth exposed to Air

A satisfactory developing bath is as follows—

Caustic soda flake	...	30 g.
Sodium carbonate (anhydrous) ...	...	25 g.
Sodium hydrosulphite	...	50 g.
Water	...	695 c.c.
Wheat starch (5% soln.)	...	200 g.
		1,000 g.

The starch should be well boiled in water before it is added to the liquor.

The quantity of pad-liquor applied to the print should not be high enough to allow free flow of liquid on the cloth; otherwise, flushing will occur. The uptake should be as low as possible consistent with complete wetting-out of the printed portions. The actual pick-up will depend on the method of padding and the type of cloth, but a figure of 70–80% (on the dry weight of fabric) is normal. For fine fabrics a lower figure, about 50%, can be used. The temperature of the pad-liquor must be kept as low as possible, preferably below 20°C., if necessary by circulating cold water through a jacket on the pad-trough.

F. STEAMING CONDITIONS AND EQUIPMENT

Experiments with the laboratory ager using a number of vat dyes having different fixation characteristics showed that a plentiful supply of saturated, air-free steam at, or slightly above, atmospheric pressure was essential for flash-ageing. It is understood that in the U.S.A. flash agers are frequently run at temperatures up to 120°C. with the object, it is claimed, of increasing the rate of reduction and fixation. In view of the very rapid rates of reduction of many vat dyes, however, it has been shown that this is not the chief use of super-heated steam. Under laboratory conditions, although no increase in rate of fixation was found with a number of vat dyes, the definition obtained from dyes in Groups III and IV (Table IV) was improved, according to their tendency to flush, owing to the drying-out of excess water picked up by the fabric during padding.

Drying-out in superheated steam can have an adverse effect on fixation if carried too far, since fixation is essentially a dyeing process requiring sufficient water for solution and diffusion of the leuco vat dye. For optimum results, therefore, careful control of running speed and temperature are necessary, and it will usually be simpler to exert such control at the padding stage and to rely on saturated steam.

Compared with conventional roller agers or festoon steamers, flash-ageing equipment is of small volume and simple design. Several types have been proposed [13, 14], and the most suitable will depend on the requirements of individual works. A flash ager should be constructed with the following aims in mind—

(1) To provide an ample supply of saturated or slightly superheated steam to both sides of the fabric

(2) To allow for a steaming time up to 20 sec. at the required running speed; e.g. for a speed of 30 ft./min. a steamer 10 ft. long is required.

(3) To preserve the printed mark and avoid contamination of the equipment by dye. This depends to a great extent on the correct choice of dye and thickening agent, but as far as the equipment is concerned, it is advisable to avoid contact of the printed side of the cloth with any part of the steamer.

The design of flash agers falls broadly into two classes, depending chiefly on the output required. For slow speeds, up to 10 yd./min., an extremely simple and inexpensive steamer is satisfactory, but higher production rates demand larger steamers, which are necessarily more complicated and expensive.

For low speeds the vertical type shown in Fig. 5 and 6 fitted to a conventional pad-mangle has given satisfactory development of machine and screen prints on a wide range of fabrics in

F	Face side of print
1	Body of ager, 5 ft. × 30 in. × 6 in.
2	Detachable end-pieces
3	Perforated steam pipes with wire gauze baffles
4	Perforated steam coil inside the mouthpiece
5	Internal lips to keep the mouthpiece dry
6	Drain for condensate
7	Guide-roller
8	Spacing bar on existing mangle
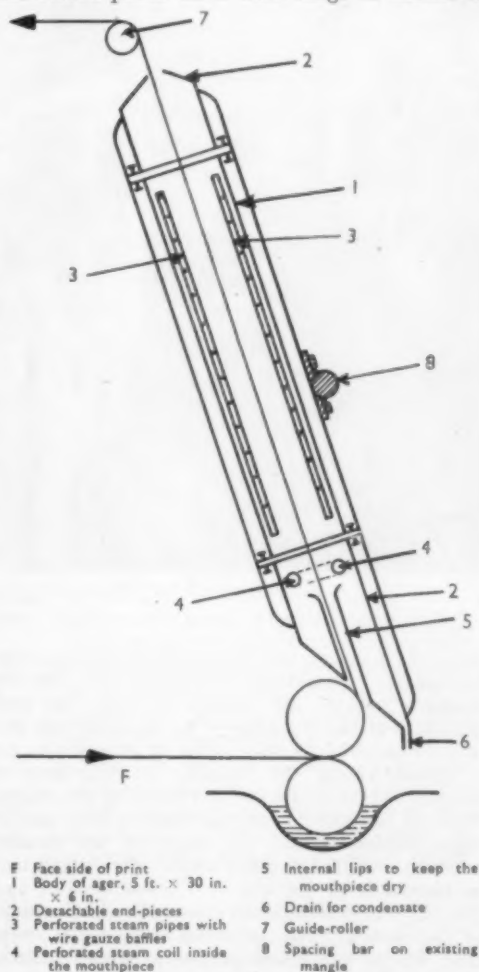
FIG. 5— Flash-ager fitted to Existing Pad-mangle

runs of up to 500 yd. at 7 yd./min. The ager consists of an efficiently lagged metal steaming chamber with no internal moving parts. By careful alignment, the cloth can be made to pass straight through the steamer without touching any part of the equipment. The vertical position avoids water-spotting from condensation, and also any necessity for supporting rollers to take up sagging

steam coils to prevent water-spotting and in which the cloth is supported on the underside by rollers driven at the same speed as the cloth. In spite of this precaution, contact with the rollers tends to draw colour through the cloth, resulting in dragging of the print and marking-off on the rollers, especially when the print is well penetrated. However, control of the liquor uptake from the
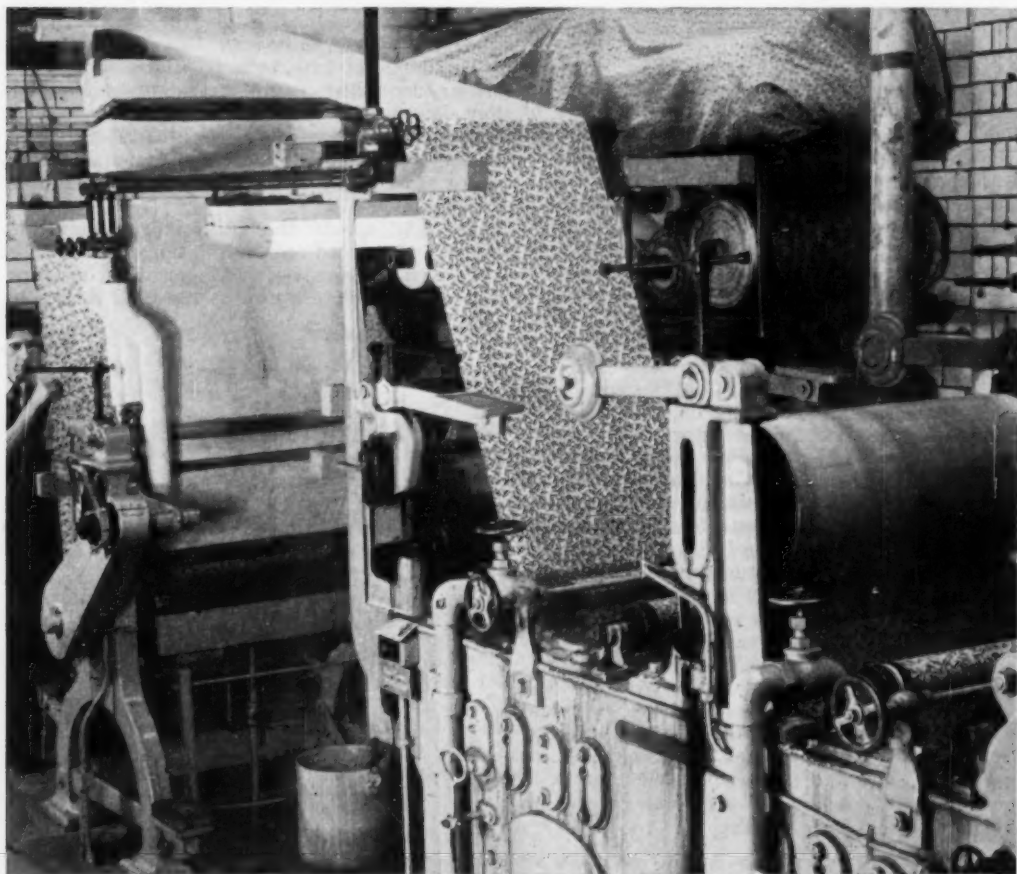
FIG. 6— Flash-ager

of the cloth, which would occur if the position were horizontal. The steamer is placed to give the shortest possible air passage between the pad-mangle and the mouthpiece to minimise the risk of hydrosulphite decomposition on exposure to air.

Within limits, the capacity of this type of steamer can be increased by increasing the length. There is, however, a practical limit to this, and for high running speeds the shape of the steamer must be modified in other ways. The length may be increased by the use of a tower type of ager (Fig. 7), which retains the essentially simple design of the vertical type, or of an "inverted-U" type (Fig. 8), the horizontal portion of which is fitted with auxiliary steam chests or heated with closed

pad-mangle and a small addition of thickening to the pad-liquor help to maintain sharp definition. The entry mouthpiece is heated by closed steam coils to prevent water-spotting.

The more complicated types of steamer become more costly, and largely defeat the main attractions of flash-ageing, viz. simplicity and low capital cost of equipment, coupled with small cloth capacity and steam consumption.

G. OXIDISING AND WASHING

After leaving the ager the cloth must be passed immediately into the clearing and oxidising baths using a conventional open-width soaping range. The first tank should contain running water to

F   Face side of print
1   Heated jacket
2   Heated inlet mouthpiece
3   Heated outlet, immersed
4   Steam inlet, with baffles
5   Support rollers, allowing
    alternative cloth route to
    vary steaming time
6   Drain for condensate
7   Insulation
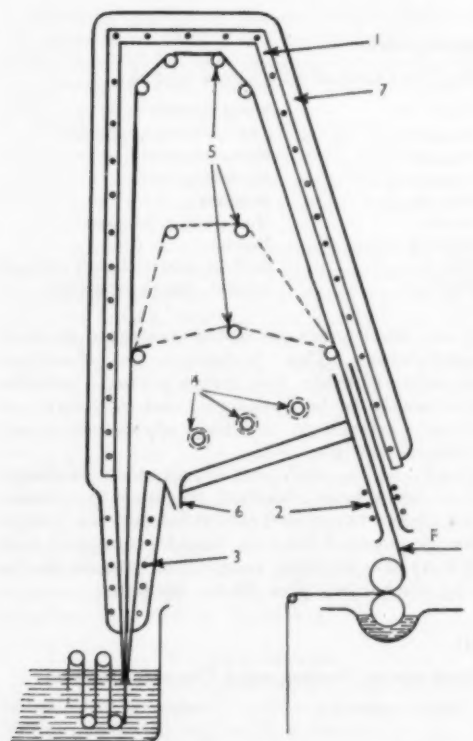
FIG. 7— Flash-ager— Vertical or Tower Type

F   Face side of print
1   Heated jacket
2   Heated mouthpieces
3   Steam inlet pipe (with baffle)
4   Supporting rollers (driven)
5   Drain for condensate
6   Insulation
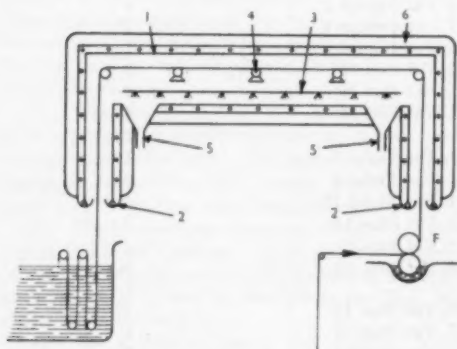
FIG. 8— Flash-ager— Horizontal

eliminate caustic alkalinity from the cloth and soften the thickening as quickly as possible. The rate of oxidation of the leuco vat dye may be increased in the following tanks by the use of oxidising agents such as sodium dichromate, sodium percarbonate, sodium perborate, or hydrogen peroxide. The brightest colours are usually obtained when oxidation is carried out with water alone. This is particularly important where—

Caledon Blue XRN	C.I. Vat Blue 4
Caledon Blue GCP	C.I. Vat Blue 14
Caledon Blue XRC	C.I. Vat Blue 6
Caledon Brilliant Blue 3G	C.I. Vat Blue 12

are used, since these dyes become duller and greener under the action of the oxidising agents mentioned above.

To develop full brightness and optimum fastness properties, the goods are finally treated at or near the boil for 5–10 min. in soap or a solution containing 2 c.c. of Lissapol NC per litre (¼ pint per 10 gal.) and 0·5 g. of soda ash per litre (3 oz. per 10 gal.), and then rinsed and dried.

H.   COLOUR AND FASTNESS

The decomposition of leuco vat dyes at high temperatures has been examined by Fox[15], who attributed it to hydrolysis (e.g. Caledon Gold Orange 3G), dehalogenation (e.g. Caledon Printing Purple 4R), or isomerism and over-reduction (e.g. Caledon Blue XRN). It was observed with many dyes fixed in 20 sec. under flash-ageing conditions that the final colour differed significantly from that normally associated with the dye when fixed for 8 min. by the all-in process. In all such cases the dyes were known to be potentially capable of one of the three changes described above. Some of the more outstanding examples are given in Table VII.

It is concluded that flash-age development is capable of giving more nearly the correct colour of those dyes which are capable of degradation when exposed to high temperatures in the leuco form.

In no respect was the fastness of a given vat dye found to be inferior by the flash-ageing process, compared with the fastness normally obtained by the all-in process.

IV— Modified Flash-ageing Processes

The development of vat prints by padding with hydrosulphite–caustic soda suffers from certain fundamental defects, the chief of which are—

(1) Instability of the pad-liquor

(2) Wastage of a large proportion of the pad-liquor where the printed coverage is small

(3) Necessity of using the same concentration of reducing agent for all vat dyes in a multicolour pattern, irrespective of their individual requirements

(4) Inability to process certain other dyes alongside vat dyes in order to increase the range of colours (e.g. direct dyes in vat-illuminated discharge styles, azoic or reactive dyes), owing to chemical attack by the reducing system.

These limitations could be eliminated by a process which depended on printing the vat dye *and* the reducing agent, and subsequently padding in caustic soda solution before steaming. Reducing

TABLE VII

Effect of Flash-ageing on Colour

(Colour after 8 sec. steaming compared with that of all-in print steamed for 8 min. as control)

Caledon Printing Yellow 6GS Paste	C.I. Vat Yellow 27	Much brighter
Caledon Printing Orange GS Paste	C.I. Vat Orange 9	Slightly redder, brighter
Caledon Printing Orange 4RNS Paste	C.I. Vat Orange 4	Much brighter
Caledon Gold Orange 3G 200 Paste Fine	C.I. Vat Orange 15	Much brighter
Caledon Red 2GN 150 Paste Fine	C.I. Vat Red 23	Brighter
Caledon Printing Purple 4RS Paste	C.I. Vat Violet 1	Much redder, brighter
Caledon Brilliant Violet 3BS Paste Fine	C.I. Vat Violet 9	Redder
Caledon Printing Blue XRNS Paste	C.I. Vat Blue 4	Slightly redder, slightly brighter
Caledon Printing Blue GCPS Paste	C.I. Vat Blue 14	Redder, slightly brighter

agents such as glucose or a ferrous salt [16], or zinc dust [17], have previously been suggested, but one of the most widely applicable is thiourea dioxide or Manofast (Hardman & Holden Ltd.) (C.I. Reducing Agent 11). In presence of caustic soda its reducing power is similar to that of hydrosulphite [18], so that the same range of dyes is applicable, and a process using this agent is being developed [19].

Although thiourea dioxide decomposes if dried at the high temperatures normally used in machine printing, it is quite stable at the slightly elevated temperatures used for drying many screen prints,

and the dried prints are stable to storage at room temperatures. This technique is, therefore, eminently suitable for screen-printed patterns subsequently to be flash-aged, and may have an economic advantage in all-vat styles where low coverages are involved.

Good white and vat-illuminated discharge effects have been obtained on direct- or azoic-dyed viscose rayon and cotton fabrics, the greater reducing power of thiourea dioxide, compared with sulphoxylate, enabling many dyed ground shades to be discharged after 20 sec. steaming.

TABLE VIII

Vat Dyes suitable for Application by the Modified Flash-ageing Process using Thiourea Dioxide

Dye	Colour Index No.	Concn. of Thiourea Dioxide (g./100 g. print paste)
Caledon Printing Yellow 6GS Paste	C.I. Vat Yellow 27	2
Caledon Yellow 5GK 150 Paste Fine	C.I. Vat Yellow 26	2
Caledon Printing Yellow 5GS Paste	C.I. Vat Yellow 2	1
Caledon Printing Yellow GNS Paste	C.I. Vat Yellow 1	1
Caledon Printing Orange GS Paste	C.I. Vat Orange 9	1
Caledon Gold Orange 3G 200 Paste Fine	C.I. Vat Orange 15	1
Caledon Printing Orange 6RS Paste	C.I. Vat Orange 3	1
Caledon Printing Orange 4RNS Paste	C.I. Vat Orange 4	1
Caledon Printing Orange 2RTS Paste	C.I. Vat Orange 2	1
QF Caledon Printing Scarlet G Paste	C.I. Vat Red 37	3
Caledon Printing Red 3B 200 Paste	C.I. Vat Red 10	2
Caledon Red 2GN 150 Paste Fine	C.I. Vat Red 23	1
FD Caledon Rubine B Powder Fine	—	2
Caledon Printing Purple 4RS Paste	C.I. Vat Violet 1	1
Caledon Brilliant Violet 3BS Paste Fine	C.I. Vat Violet 9	2
Caledon Violet XBNS Paste Fine	C.I. Vat Violet 13	2
Caledon Printing Blue GCPS Paste	C.I. Vat Blue 14	0·5
Caledon Blue XRCS Paste Fine	C.I. Vat Blue 6	2
Caledon Printing Blue 3GS Paste	C.I. Vat Blue 12	0·5
FD Caledon Blue 3RC Powder Fine	—	2
Caledon Printing Navy GS Paste	C.I. Vat Blue 16	2
Caledon Printing Dark Blue 2RS Paste	C.I. Vat Blue 17	1
Caledon Printing Jade Green XBNS Paste	C.I. Vat Green 1	2
QF Caledon Printing Jade Green XBN Paste	C.I. Vat Green 1	1
Caledon Printing Jade Green 2G 300 Paste	C.I. Vat Green 2	1
Caledon Green 7G 200 Paste Fine	C.I. Vat Green 16	2
Caledon Printing Olive Green BS Paste	C.I. Vat Green 3	2
Caledon Printing Green 6BS Paste	C.I. Vat Blue 7	1
Caledon Printing Brown 4RS	C.I. Vat Brown 28	2
Caledon Printing Grey BS Paste	C.I. Vat Black 24	1
QF Caledon Printing Black 2R Paste	—	2
QF Durindone Printing Pink FF Paste	C.I. Vat Red 1	0·5
QF Durindone Printing Magenta B Paste	C.I. Vat Violet 3	1
QF Durindone Printing Red 3B Paste	C.I. Vat Violet 2	1
Durindone Printing Brown GS Paste	C.I. Vat Brown 5	2

Preliminary experiments show that it should also be possible to print vat dyes alongside azoic or reactive dyes by this method, provided that a small-volume pad trough is used to prevent build-up of reducing agent.

Finally, it is possible to adjust the concentration of thiourea dioxide according to the requirements of individual vat dyes, so that each component of a multicolour print gives its optimum brightness and maximum colour value.

The general details concerning thickening agents and padding and steaming conditions already given for the hydrosulphite process apply equally to the thiourea dioxide method. The starch–gum Gatto-alginate thickening can be kept as a stock thickening, the required amount of thiourea dioxide being added to the individual print pastes as a 25% (wt./vol.) paste milled in water. The padding solution for the Manofast process is prepared exactly as for the hydrosulphite process, but omitting the hydrosulphite. The caustic alkaline developing bath is stable, and any quantity can be made up and stored till required. Steaming, oxidising, and washing are exactly as described for the hydrosulphite process. A list of suitable dyes, together with the concentration of Manofast required, is shown in Table VIII.

V— Conclusions

(1) The hydrosulphite–caustic soda system is potentially capable of reducing all vat dyes at 100°c. Flash-ageing, with a steaming time of 20 sec., is a practicable process for developing vat-printed cellulosic fabrics provided that precautions are taken to ensure the correct choice of thickening agent, dye, and padding and steaming conditions. The choice of suitable dyes is limited by the rate of reduction, which must be rapid enough to permit almost complete reduction in the steaming time employed, or by the affinity of the leuco dye for the fibre, which must be great enough to eliminate lateral diffusion from the printed mark during steaming.

(2) The choice of suitable dyes for the flash-ageing process is greater on viscose rayon than on cotton, since the leuco vat dyes tend to have a higher substantivity for viscose rayon and, consequently, flush to a much smaller extent.

(3) The percentage fixation of dyes on viscose rayon is higher than on cotton when steamed for 20 sec., and the fixation by flash-ageing generally is at least as good as by the all-in method, where steaming is for 8 min.

(4) The colour of many vat dyes is brighter when fixation is by flash-ageing owing to the shorter exposure of the leuco dye to high temperatures.

(5) Water-in-oil emulsion thickenings are considered not to show marked advantages in the flash-ageing process over conventional polymeric thickeners.

(6) A large-scale flash ager, capable of running at a modest speed with a steaming time of 20 sec., can be constructed cheaply and gives excellent results with a wide variety of cellulosic fabrics provided that the correct choice of thickening agent, dye, and fixation conditions has been made. Such a process should be of considerable interest to screen printers, and to machine printers who wish to extend their steaming capacity for all-vat styles.

(7) By suitably modifying the normal flash-ageing process, and incorporating thiourea dioxide in the print paste, it should be possible to use vat dyes alongside azoic or reactive dyes, and in illuminated discharge styles. There may also be an economic advantage in using this reducing agent if the printed coverage is small.

* * *

Some of the experimental work described in this paper was carried out by Mr. A. Bari.

DYEHOUSE DEPARTMENT
  IMPERIAL CHEMICAL INDUSTRIES LTD.
    DYESTUFFS DIVISION
      HEXAGON HOUSE
        MANCHESTER 9

References

[1] Thornton and Liquorice, *J.S.D.C.*, **72**, 472 (1956).
[2] *Bull. Soc. ind. Mulhouse*, **95**, 221 (1929): Koechlin Bros., Sealed Communication of 30th December 1911.
[3] IG. Farbenindustrie AG., *BP* 279,864 (1928), *BP* 297,959 (1928).
[4] Idem, *BP* 304,787 (1930).
[5] Michie and Thornton, *J.S.D.C.*, **69**, 629 (1953).
[6] DuP, *USP* 2,587,905 (1952).
[7] Saville, *Amer. Dyestuff Rep.*, **44**, P 105 (1955).
[8] Diserens, *Chemical Technology of Dyeing and Printing*, (New York: Reinhold Publishing Corpn.), **1**, 33 (1948).
[9] DuP, Technical Monograph, *Savagraph Vat Emulsion Printing Process* [No date], 5 pp.
[10] Marshall and Peters, R. H., *J.S.D.C.*, **69**, 583 (1953).
[11] Idem, *ibid.*, **68**, 289 (1952).
[12] Fowler, Michie, and Vickerstaff, *Melliand Textilber.*, **32**, 296 (1951).
[13] Tower Iron Works, *BP* 742,207.
[14] British Cotton Industry Research Association, *Dyer*, **117**, 36 (1957).
[15] Fox, *Hexagon Digest*, No. 10, 3 (Oct. 1951); *J.S.D.C.*, **65**, 508 (1949).
[16] IG., *BP* 314,904 (1930).
[17] Steinlé, *BP* 775,820 (1957).
[18] Krug, *J.S.D.C.*, **69**, 606 (1953).
[19] Since this paper was submitted to the Society of Dyers and Colourists we have become aware of Scott Bader & Co.'s patent *BP* 780,803, the complete specification of which was published on 7th August 1957. This describes and claims the printing process which forms the subject of § IV of this paper.

Discussion

Mr. H. A. TURNER: Can the stabilisation of hydrosulphite to oxidation reported in this paper, and effected by the addition of thickening agents to the reducing bath, be ascribed to either (*a*) the association of thickeners with the hydrosulphite, since some at least have aldehyde groups in the molecule, or (*b*) the slight buffering effect of these polyglycol compounds on the alkali?

Mr. FERN: We have interpreted the stabilising effect of thickening agents on hydrosulphite in padding liquors as due to the decreased rate of diffusion of oxygen from the air into the bulk of

the padding liquor. Several chemically different thickening agents give almost the same protective effect, and this would not easily be explained by suggestion (*a*). As for suggestion (*b*), we think that the buffering effect of these thickening agents on a 5% sodium hydroxide solution would be negligible. Support for slower access of air as the explanation comes from Dr. W. Furness (see below). We confirm that there is nothing inherently unstable in a padding liquor composed of sodium hydrosulphite and sodium hydroxide provided that it can be protected from the atmosphere.

Dr. W. L. Lead: Have experiments been made with any other aldehydic stabilisers? It is known, for example, that sodium acetaldehyde-sulphoxylate is much more stable at room temperature to atmospheric oxidation than is sodium hydrosulphite, whilst at temperatures near 100°c. it develops its full reducing power.

Mr. Fern: No experiments have been carried out with sodium acetaldehyde-sulphoxylate in this programme of work on flash-ageing. From Dr. Lead's description of its properties it would seem an interesting compound to examine. The question of economics on the large scale must obviously determine whether such a product can be used successfully in competition with sodium hydrosulphite and a small amount of a cheap thickening agent. It should also be remembered that the thickening agent is necessary in any case, since it ensures a satisfactory degree of pick-up of pad liquor by the fabric.

Dr. W. Furness: The data for Fig. 4 were obtained by padding, exposing to air, immersing the fabric in iodine solution, and then determining analytically the quantity of iodine reduced. It is seldom that this procedure affords an accurate measure of the amount of sodium hydrosulphite which has been oxidised, because the principal product of oxidation is sodium sulphite, and this itself reduces iodine. The general conclusions drawn by the authors are, of course, valid, because their intention was merely to compare the stabilising effects of various thickening agents. If an accurate analysis were desired in another investigation, it would be better to immerse the exposed fabric in formaldehyde solution so as to convert the residual hydrosulphite to formaldehyde-sulphoxylate, and then to determine the latter iodimetrically.

Mr. Fern: We are very grateful to Dr. Furness for his description of the more accurate method of determining sodium hydrosulphite which has undergone partial oxidation. We shall certainly adopt this procedure in any further investigation of a like nature.

Dr. Furness: With reference to § IV (1) and (2), there is nothing inherently unstable in a padding liquor composed chiefly of sodium hydrosulphite in a strongly alkaline solution. In most instances any decomposition is due to oxidation, and if such liquors can be protected from the atmosphere they will remain stable for quite a long time.

Mr. Fern: This confirms our reply to Mr. H. A. Turner's question (above).

Mr. G. S. Hibbert: Have the authors experienced trouble through loss of colour yield in any heavy spongy cloths, which might be expected to carry excess of air into the ager, and if so, has thickening the padding liquor assisted in overcoming this trouble?

Mr. Liquorice: Very little experience has been obtained on heavy spongy fabrics, but so far no difficulties have been observed with such structures. The large-scale steamer in use is of such low volume that it is relatively easy to eliminate traces of air brought into the ager by increasing the rate at which steam is introduced. With correct choice of padding conditions and the ability to regulate steam flow, we would anticipate no problems on such fabrics.

Mr. W. L. Langton: What are the relative advantages of the two methods of applying the reducing pad liquor— total immersion as against pick-up from the bottom roller?

Mr. Liquorice: No hard-and-fast rules can be laid down for determining the method of padding fabric in the flash-ageing process. Much depends on the fibre, the fabric construction, the weight of cloth, the running speed, and the nature of the design, i.e. whether the coverage is high or low and whether the fabric is screen-printed or machine-printed. In general, however, nip-padding would be used for fabrics of very light construction, where penetration of the pad liquor through the fabric is relatively easy. On the other hand, for very heavy fabrics it will be necessary to resort to total immersion in order to obtain adequate wetting-out by the padding liquor during the short time of passage through the trough. Total immersion will probably be more widely used than the nip-padding method for the majority of fabrics.

Mr. Hibbert: Have the authors considered the practical difficulty of harnessing an open soaping machine to a small ager running at 7, 10, or even 20 yd./min., and is there any possibility of interrupting the process by piling into wagons after ageing?

Mr. Fern: The difficulty mentioned by Mr. Hibbert is appreciated, and an experiment has been carried out in which printed-and-aged fabric was piled down under conditions which might be experienced if 1,000 yd. of fabric were allowed to stand for up to 1 hr. before being washed off. With machine-printed cotton and viscose rayon, little difficulty is envisaged if this state of affairs occurs. With screen-printed fabric, particularly if there are large areas of heavy colour, marking-off might be experienced if the fabric comes from the steamer with too much moisture. If it were necessary to pile down before washing off in such a case, the use of superheated steam might be an advantage. It should be noted that a complete open soaping range is not essential to oxidise vat-printed fabrics sufficiently to prevent marking off if they are piled down before the soaping stage. A simple two-beck cold-water range, fitted if possible with spurt pipes, would be adequate after flash-ageing to give the necessary degree of oxidation. Soaping could then be carried out in open width or in rope form at a convenient time.

The Migration of Dyes in the Fibre-substance during Steaming

H. B. HALLOWS and H. A. TURNER

An account is given of the examination in cross-section of sheets of fibre-substance— cellulose and secondary cellulose acetate— which have been steamed for various times in contact with a layer of thickening agent containing a dye. A variety of dyes have been used, and, from the examination, some information about the migration of dye in both thickening agent and fibre-substance film has been obtained. With some of the cross-sections an attempt has been made to measure quantitatively the distribution of dye within the fibre substance at various times of steaming, and hence to deduce the diffusion characteristics.

Introduction

A number of studies have previously been made of the migration behaviour of water-soluble dyes or water-soluble forms of dyes in a textile print during steaming. For this purpose an idealised system has been used with one or two variations [1]. In this system the fibre is represented by a film of fibre-substance of standard dimensions, and the impression by a film of dry thickening agent containing the dye and any necessary chemicals. As has been explained on previous occasions, this device allows the partition of dye at various stages of its migration during steaming to be estimated colorimetrically, since the two phases are not difficult to separate. A modification of the original method, in which wet printing paste is spread on a film of fibre-substance and dried down before steaming, follows most textile-printing processes more closely and allows migration during an intermediate drying process also to be studied [2].

This procedure was recognised from the beginning to have other advantages, because it is possible, by taking cross-sections of either the system as a whole (thickener–fibre-substance) or of the fibre-substance only, to observe the course of migration of the dye into the fibre-substance during drying or steaming. This procedure is analogous to that used in various investigations of the penetration of dye into fibres during dyeing from simple aqueous baths. Vickerstaff [3] has illustrated the kind of result obtainable in this way with a nylon monofil of relatively large diameter, and the films used in this work share with the monofil the absence of the very complex histological structure found in most natural fibres.

In general, the cross-sections of, say, cellulose films, examined before migration had reached an equilibrium condition, showed what had been expected, viz. that the concentration of transferred dye was highest in the region near the surface of contact with the thickener, and that it diminished progressively on passing deeper into the fibre. With dyes having a relatively great affinity for the fibre-substance, the "front" of the dye as it diffused into the fibre was sharply defined (Fig. 1 and 8); i.e. the concentration gradient of the dye measured from the outside to the inside of the fibre was high, whereas for low-affinity dyes the front

was diffuse, the concentration gradients being lower (Fig. 9 and 10).

In all the systems previously examined in this way, there was no definite indication that a corresponding concentration gradient could be set up in the direction of migration in the thickener phase. As the thickener was mostly a natural starch, the film was often structurally heterogeneous, but "layer" differences in dye concentration never seemed to be present. The implications of this preliminary conclusion are twofold— (a) in steam the thickener swells so much more than the fibre-substance that the mobility of dye in it is much greater; (b) in spite of the fact that both thickener and fibre are usually carbohydrates, the affinity of the dye is much less for thickener than for fibre. It is possible that both deductions are correct, and (b) is confirmed by observations of the transfer of direct dyes from starch to cellulose, where exhaustions of the order of 70% and higher can be reached. In these systems, however, a "layer" distribution of dye in a starch phase is not the inevitable result of orthodox dye migration during steaming, for the starch itself is chemically heterogeneous. There is at least the possibility of fractionation, the amylose portion tending to be absorbed on the cellulose surface. This phenomenon has been invoked by Möller [4] to explain the fact that, in printing with vat dyes, a greater superficial exhaustion but a lower fastness are obtained with starch than with gum as thickener.

It was decided to make a more systematic qualitative examination of migration in various application classes of dye employed in printing, and from this to determine how far observed behaviour corresponded to some of the important technical printing properties.

At a later stage, by the application of a simple system of micro-absorptiometry to the optical projection of the cross-sections, an attempt was made to define this behaviour in quantitative terms.

Experimental

PREPARATION OF SPECIMENS

In this work, preparing dye-containing films of thickener, bringing them into contact with films

of fibre-substance, and steaming the two in contact with each other were all performed in the same way as corresponding operations described in previous papers [5]. In general, also, the preparation of cross-sections for examination was on orthodox lines and calls only for brief comment.

CUTTING CROSS-SECTIONS

The microtome was the M.S.E. sledge pattern with a slightly hollow-ground blade (Wilkinson Sword Co.). These blades are very hard and require careful preparation but then keep their edge very well. Sharpening was on a very fine-grained water-stone, and then on plate glass with levigated alumina (6 hr. suspension). After a specimen had been steamed, it was taken without separation, dried, and at once embedded in wax (90% high-m.p. paraffin + 10% beeswax). After cooling, the cast blocks were kept for some hours in a thermos jar with ice.

The block was mounted in the microtome with the plane of the films vertical, and trimmed so that as much of the supporting wax as possible was removed from the side which met the blade first. More wax was left on the opposite side. In this microtome, the specimen holder moves and the knife is stationary. The edge of the knife was inclined at 50° to the line of movement of the specimen. The long axis of the cross-section of film was also set parallel to the edge of the knife. The blade was set so that its lower plane was as nearly horizontal as possible, being inclined just sufficiently to clear the specimen.

In general, the thickness of the sections was 60 μ. Thinner sections did not show variations in dye concentration with sufficient clearness. Thicker ones were unstable and turned over on clearing and mounting. It was absolutely essential for the film to be cut so that the side faces of the section were strictly at right angles to the plane of the cut, as otherwise both the outer edges of the image and the line of separation between the phases were badly defined. At first an attempt was made to keep the phases in contact during cutting and mounting, but often they separated a little, and this was not found to be a disadvantage. Illumination had to be critical and strictly parallel to the microscope axis, as otherwise troublesome reflections from the interphase surface into the phases themselves were encountered.

MOUNTING

The wax sections were laid on a slide prepared in the usual way with Mayer's albumen, and the embedding medium was cleared by melting in an oven at 110°c. and immersing in pure sulphur-free xylene for 5 min. The product was, in turn, cleared in 95% ethanol, and the slide dried at room temperature. The sections were then mounted as described below under a cover-glass 0·13–0·17 mm. thick.

The usual procedure, by which the mountant is chosen to have a refractive index adjusted to that of the specimen, calls here for some compromise. In all except a very few experiments the fibre-substance was either regenerated cellulose (as represented by Cellophane) or secondary cellulose

acetate. The specimens always contained also a section of a thickener layer, of different refractive index from the fibre-substance. It was impossible, therefore, to find a mountant that would be equally appropriate for the two phases. When specimens were to be viewed or photographed, it was effective to have the refractive index of the mountant slightly below that of the section, otherwise outlines did not show with sufficient distinctness. In some of the photometric work the suppression of outline detail became desirable. For relatively rapid mounting, which was an advantage towards the end, a liquid mountant, which would require the preparation to be ringed, was avoided and a resin mountant used. For cellulose (n = approx. 1·532) Euparal (Flatters & Garnett, n = 1·500) was suitable for the photographic work, and Canada balsam (n = 1·530) for the photometric. With cellulose acetate only photographic work was done, and, although the refractive index is below that of Euparal, the latter served for the few preparations made with this fibre-substance. In some later work, with insoluble azo dyes in cellulose, evidence was obtained that the terpene thinner used for Euparal could diffuse into the specimen and affect the distribution of the dye. This occurred only during long exposures to the condensed beam of the illuminant and gave no trouble in the present work.

PHOTOGRAPHY

A Watson Bactil microscope, of tube length 160 mm., with achromatic lenses, was arranged along a vertical axis with a long-extension camera. The illuminant was a 30-watt 6-volt condensed-filament lamp in a suitable housing, with a filter-carrier and auxiliary iris. Where marked contrast was desired, filters of Cellophane dyed with a dye selected to give complementary light transmission were employed. The condenser was adjusted for critical illumination. Generally speaking, a magnification of 88 diameters as determined with a stage micrometer (objective $\frac{2}{3}$ in., eyepiece × 4) gave images of convenient size. The image was well masked to occupy only the centre of the projected field. The plate was Kodak P 300, a backed, fine-grain, medium-speed panchromatic plate (Weston 20, Log Exposure Index No. 24° in artificial light). High-contrast developers are unsuitable for this work, and a medium-contrast metol–hydroquinone developer was employed, time and temperature development being adjusted to obtain the γ value close to 0·8. Prints were made on white, smooth, glossy, Velox (Kodak) gaslight paper.

MICROPHOTOMETRY

This was carried out, as will be explained later, on specimens obtained by steaming for different times with pure Chlorazol Sky Blue FF (C.I. Direct Blue 1) in potato-starch, in contact with Cellophane. The sections were prepared and mounted as above, and projected in the same way into the camera.

After focussing, selecting the specimen, and adjusting the position of the image, the focussing screen was removed and replaced by an assemblage which held a metal casing containing a nine-stage

photomultiplier (type 931 A)[6]. Light entered this from the projected image through a slit ultimately fixed at 10 mm. long by 0·0051 mm. wide. The flat plate in which the slit was cut was in the plane of focus, and the whole could be traversed along this plane by an accurately cut lead screw turned by a calibrated drum. With the image of the Cellophane section arranged with the long axis coincident with the length of the slit, it was possible to carry out about 70 readings as the slit was traversed in steps across the image of the section. Some backlash in the screw was allowed for by traversing in one direction only during an actual determination. There was no creep of the screw.

The output from the photomultiplier was carried by heavily screened leads to a micro-photometer Type 117 A (Harwell) fed by a stabilised high-voltage power pack 1007 (Harwell)[6]. For circuits and characteristics of these instruments the original references should be consulted. The microphotometer requires light incident on the photomultiplier to be modulated at approx. 100 cycles/sec., and this was done simply and directly by interposing in the illuminating beam, between the iris on the lamphouse and the micro-scope, a strip of black metal with its long axis attached directly to the shaft of a synchronous motor (Hoover ⅛ h.p.). By suitable masks, it was arranged that complete obscuration of the beam just occurred when the plane of the strip was at right angles to the optical axis. The rated speed of the motor was 2,850 r.p.m., thus giving a true sine-wave modulation of 95 cycles/sec. Constant-voltage regulators were used to feed both the light source and the motor. There was a slight rhythmic change of speed in the motor, which showed itself as a regular fluctuation about a mean position in the indicating meter of the spectrophotometer. This did not prove to be objectionable. Comments on the performance of the photometer will be given when the results are considered.

Results and Discussion
Qualitative Investigations
GENERAL

As previously noted, dyes which are intrinsically water-soluble and undergo no visible change in their state of aggregation during steaming diffuse as might be expected. When examined after increasingly long steaming times, they are seen to progress further into the layer of fibre-substance from the layer of thickening agent, until ultimately a uniform and intense coloration of the former is established. When there is marked affinity of the dye for the fibre, the "front" of the region occupied by the diffusing dye is sharply defined. It is not possible in this paper to reproduce the many photographs which were taken as evidence for this behaviour, but the simple transfer of a direct dye, Chlorazol Sky Blue FF (C.I. Direct Blue 1) (Fig. 1) may represent this straightforward behaviour. On the other hand, the transfer of a vat dye in a system which represents the ordinary Formosul–potash style shows quite obviously the reduction

and solubilisation of dye particles in the starch layer as a preliminary to transfer (Fig. 5). The persistence of the sparingly soluble dye particles in the thickener layer until all have finally passed into solution and migrated into cellulose acetate is shown very clearly with disperse dyes (Fig. 7).

Behaviour of this kind is fairly easy to predict. That of the low-affinity dyes (e.g. levelling acid dyes of low molecular weight in cellulose), which disperse and diffuse quickly, may prove to be more interesting, since the freedom to diffuse is not controlled by affinity to the same extent. It should be remembered that, besides the initial cause of diffusion, viz. the difference in dye concentration between the thickener and the fibre phases, there are two other regions in the system where phenomena which influence dye distribution can occur. These are, respectively, the outer surface of the thickener and that of the fibre-substance, both in direct contact with steam, and therefore prone, for some periods at least, to be more swollen than the rest of the phase. This condition should encourage diffusion into them from the inner portions of the phase. Where dyes are surface-active, this property may also lead to accumulation in the surface regions. The migration of insoluble azo dyes to the outside of the fibre on soaping is a well known phenomenon.

Some secondary disturbances to the main course of diffusion have already been indicated by the behaviour of the acid dyes in their partition between starch and cellulose[2]. With these general objectives in mind, we may now describe the behaviour of representative members of different application classes.

DIRECT DYES
From Starch to Cellulose

Here, work has largely been on the migration of dye between a starch thickener and regenerated cellulose. The photographs (Fig. 1) are a selection from a more detailed series and reveal at once the following features, none of which is unexpected but few of which have been demonstrated before. The dye Chlorazol Sky Blue FF (C.I. Direct Blue 1), originally freed from electrolyte, represents a multivalent direct dye of very moderate aggre-gating powers, high salt sensitivity, and therefore fairly high substantivity for cellulose when present at the relatively great concentrations which are set up in the system during the uptake of limited proportions of water from steam—

(*a*) The good solubility of the dye is shown by the substantial absence of discrete particles of dye in the starch layer even at zero steaming time. The large-scale markings shown in the photographs of the starch phase are artifacts and arise from certain difficulties encountered in cutting and mounting the sections.

(*b*) The high dye affinity is shown by the slow and steady progress of the dye into the cellulose layer, with a sharp and well defined front as steaming continues.

(*c*) According to the photographs, the dye becomes uniformly distributed within the cellulose layer in 120 min. Corresponding determinations

of dye partition show that the exhaustion at this time is 65·3%. Steaming for 240 min. and 480 min. leads to exhaustions of 69·6% and 68·7% respectively.

(d)   After steaming for these longer times (240 and 480 min.) there is evidence, however, that the starch layer in the vicinity of the interphase surface is becoming denuded, pointing perhaps to the fact that the proportion of highly mobile dye remaining in the starch is now small and that dye diffusing into the cellulose layer has to come from a supply which is already bound by its affinity for the starch. Visual inspection suggests also that there is appreciable migration of dye to the outer face of the starch, an effect which is not clearly brought out in photographic reproductions.

(e)   The time of half-exhaustion (35%) is about 16 min. from the commencement of steaming. The time taken for dye to reach an appreciable concentration locally (i.e. disregarding the very weak fringe preceding the main front) at a point half-way through the cellulose is just under 60 min. This shows that a "strike" mechanism can operate under printing conditions also. This is confirmed by the formation of a very narrow intense layer of colour just inside the interphase boundary on the cellulose side in less than 5 min.

A similar series of preparations was made which in some respects may be considered to correspond even more closely to the actual operation of printing than that just discussed. As explained in previous papers, in order to have stable and reproducible conditions in the experimental system, the thickener, corresponding to the impression, was prepared separately from the fibre-substance by drying down a defined layer of printing paste on glass to a solid film. This was then pressed against a water-swollen layer of Cellophane, which had been kept in water for some days also to bring it to a stable condition.

In the variant, a layer of printing paste was spread directly on the water-swollen Cellophane, and the two were dried together at room temperature. Steaming then took place, as required, with pieces of the dried combined films. The ultimate results of this steaming were very much as already described, but the following differences were observed—

(a)   Drying at room temperature before steaming caused a very thin strike of dye on the cellulose, corresponding to about 10% exhaustion.

(b)   Steaming for almost 30 min. was required before the dye appeared to diffuse very much further into the cellulose.

(c)   The final exhaustion was only of the order of 45%, reached in 480 min. Half-exhaustion, to include the dye already transferred during drying, took place after 15 min. steaming. Penetration half-way through the cellulose layer required about 150 min.

(d)   Gradients in the dye concentration in the starch layer became marked only after 300 min.

These observations show the great assistance afforded by a preliminary swelling of the Cellophane to the transfer and migration of the dye.

In comparable experiments in which the thickener layer contained sodium chloride to the extent of five times the weight of dye, the presence of salt had little distinctive effect on the general features of migration and penetration, although at any given time the exhaustion was higher (81% at equilibrium, half-exhaustion time approx. 8 min., half-penetration time again about 60 min.). Local denudation of the starch layer shows itself earlier (60 min.). This may be purely an optical impression, since there is less dye present, or it may be a consequence of stronger fixation of residual dye by the starch.

A surprising observation in this series was that the starch films were thinner than those prepared without addition of salt, although it must be remembered that dry sections were being examined. Other work has shown that the presence of electrolyte, as expected, increases the uptake of water by starch from steam.

From Cellulose to Starch and to Cellulose

Although not directly relevant to the main problem of dye fixation in printing, an opportunity was taken of using this method to demonstrate the mechanism of levelling of a direct dye on cellulose during steaming. For this purpose "desorption" experiments were carried out in which dye-containing Cellophane was steamed in contact with (i) a film of starch containing no dye and (ii) a second sheet of undyed Cellophane. The results of (i) are not illustrated, but served to show the low affinity of starch relative to that of cellulose, the equilibrium exhaustion to the starch being reached after about 400 min. and then amounting to about 17%. At no stage in the transfer were concentration gradients of dye visible either in the cellulose or in the starch. To establish this point decisively would need accurate microcolorimetry, for small differences are not, apparently, perceptible in the relatively high concentration of dye in the cellulose, and the small amount of dye released to the starch diffuses rapidly throughout the layer. This is also a graphic demonstration of the effect of affinity on the rate of diffusion.

The migration of the same dye from dyed to undyed Cellophane is shown in Fig. 2 and presents some interesting features—

(a)   An almost ideal result is attained, exhaustion from dyed Cellophane to undyed being 48·2% in 240 min. and 52·9% in 480 min. The dye in the coloured layer was introduced not by orthodox dyeing but by equilibrium transfer from dye-containing starch (480 min. steaming). The two films of Cellophane had not, therefore, identical histories, since the coloured one, at the end of the experiment, would have been in steam for a total time of 960 min., the initially uncoloured one for 480 min. This alone could probably account for an exhaustion above 50%.

Migration of Dyes between Substrates

In all cases except Fig. 3 (Desorption) migration of dye is from left (thickener) to right (fibre substance) after steaming for the time specified
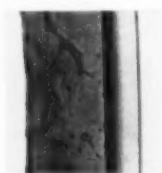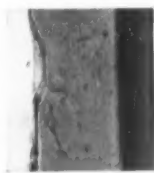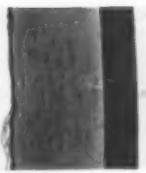
| 15 min. | 60 min. | 120 min. | 240 min. |

FIG. 1— Chlorazol Sky Blue FF from Starch to Cellulose
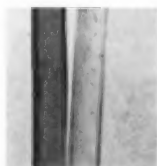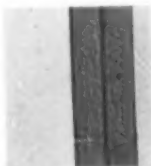
| 60 min. | 240 min. |

FIG. 2— Chlorazol Sky Blue FF from Cellulose to Cellulose
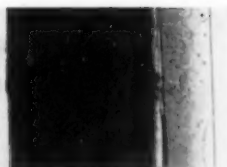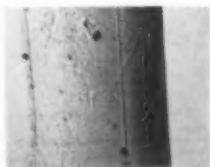
| 60 min. | Absorption | 240 min. | 60 min. | Desorption | 240 min. |

FIG. 3— Chlorazol Sky Blue FF between Cellose PC 450 and Cellulose

5 min.

FIG. 4— Chrysophenine G from Starch to Cellulose
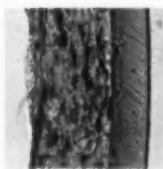
| 30 min. | 30 min. |
| Low   alkali concn. | High |

FIG. 5— Durindone Blue 4 BC from Starch to Cellulose
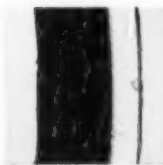
| 5 min. | 30 min. |
| Low   alkali concn. | Low |
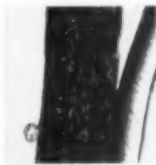
FIG. 6— Caledon Jade Green XN from Starch to Cellulose

Migration of Dyes between Substrates

Migration of dye from left (thickener) to right (fibre substance) after steaming for specified time

Before   15 min.   60 min.   240 min.
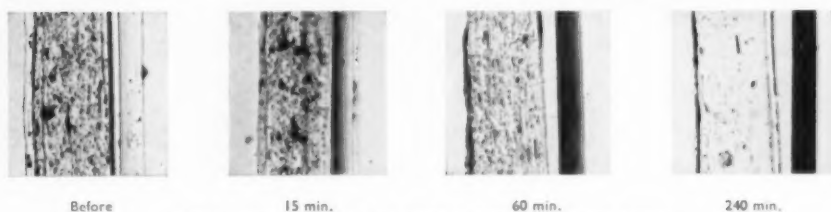
FIG. 7.— Duranol Red 2B from Starch to Secondary Cellulose Acetate

60 min.   60 min.   60 min.
—   + NaCl   + NaCNS
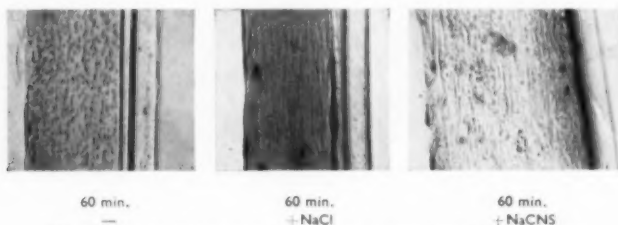
FIG. 8— Solacet Fast Scarlet B from Starch to Secondary Cellulose Acetate

20 min.   40 min.   60 min.
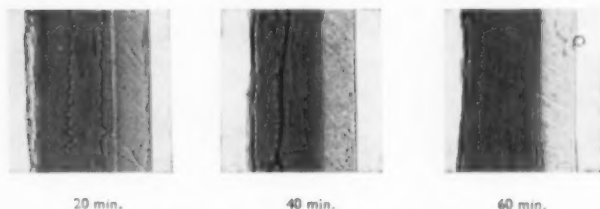
FIG. 9— Coomassie Brilliant Blue FF from Starch to Cellulose

Before   20 min.   60 min.
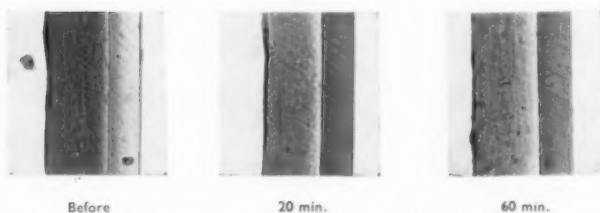
FIG. 10— Naphthalene Red EA from Starch to Cellulose

5 min.   30 min.   60 min.

Without Chromic Acetate

5 min.   30 min.   60 min.

With Chromic Acetate

FIG. 11.— Azol Printing Red R extra from Starch to Cellulose

(*b*) This series demonstrates what occurs when the phase which corresponds to the thickener layer consists of a substance which has an affinity comparable with that of the fibre and in which there is also a comparable rate of diffusion. Although dye has penetrated to the outer face of the receiving film at 60 min., there is still a concentration gradient across this film. The gradient seems almost to have disappeared at the end of 240 min., although dye continues to build-up in this layer for a further 120 min.

(*c*) In contrast to what is observed with starch, no concentration gradient is visible in the original dye-containing layer at any time, presumably because water-uptake and swelling are the same in the two layers and also because movement is, in any case, not so rapid as in starch.

Migration between Cellulose Ethers and Cellulose

The study of the influence of the relative affinities of the thickener and fibre-substance layers was completed by taking a commercial cellulose ether preparation (Cellose PC 450), readily soluble in cold water, sparingly soluble in hot, as the thickening agent. Transfer from this thickener to Cellophane was very slow compared with that from starch, and even as equilibrium was approached, exhaustion did not much exceed 20%. Therefore a greater proportion of dye was used (three times the amount per unit area) than with starch. Further, because of the lower concentration of solid matter required to produce a paste of workable viscosity, the original paste was made more dilute than the starch paste, and the thickness on spreading was correspondingly increased. This paste requires to be placed under vacuum before it is spread, because it holds air bubbles very tenaciously.

With the small proportion of dye transferred (Fig. 3), equilibrium exhaustion is attained between 120 and 240 min. steaming, and half-penetration requires about 60 min. In this respect there is no great difference from the mode of transfer from starch films. With the large proportion of dye initially present in the cellulose ether phase, any concentration gradients in this phase are impossible to detect, especially as the exhaustion is low.

Desorption from coloured Cellophane into Cellose PC 450 is very different from desorption into starch, being more like desorption into cellulose itself. Surprisingly, this desorption at equilibrium is high (67% in 480 min.), although in this case the diffusing front is not sharply defined. Penetration of dye through the Cellose PC layer takes place in 120 min., although build-up of dye continues for another 240 min. (Fig. 3).

In previous work on the transfer of direct dye from cellulose ether to cellulose, the low exhaustion has been ascribed to insolubilisation of the ether in the steam, resulting in a limited water-uptake and a correspondingly slow migration from the ether layer[7]. It is evident that this view must be revised, and that cellulose ether thickeners of this

kind have an intrinsic affinity for direct dyes, exceeding that of regenerated cellulose itself.

In the work with Cellose PC 450 it was found that the cellulose layer, as it finally appeared in the mounted cross-section, was always thicker than the same kind of regenerated cellulose after it had been steamed in contact with starch. This effect was traced to swelling, brought about in mounting, by the moisture contained in the Meyer's albumin. There are some unusual features of this observation which are not easy to explain.

Migration of Chrysophenine G
(*C.I. Direct Yellow 12*)

In the transfer of Chrysophenine G (C.I. Direct Yellow 12) from starch to Cellophane the exhaustion is low and is particularly sensitive to the relative weights of the two phases, since, with the same thickener film, equilibrium transfer to 600 PT Cellophane is 20% and that to 300 PT Cellophane (half the thickness of the 600 PT grade) is very close to 10%. Diffusion is very rapid, substantially complete penetration of the cellulose film requiring just over 5 min. steaming (Fig. 4).

An unusual observation with this dye is the marked graining of the starch film, a phenomenon not observed with Chlorazol Sky Blue FF (C.I. Direct Blue 1). This appears to be due to an actual heterogeneity in the starch structure and not to separation of solid dye particles. Whether there are special steric relations between this dye and starch dispersions has not yet been ascertained, nor whether there is a separation of starch into fractions (say rich in amylose and amylopectin respectively) accompanied by differential staining. With this dye a complementary filter is needed to distinguish between changes in concentration of dye in the cellulose. The resulting high contrast may thus render this structure unusually easy to observe.

VAT DYES FROM STARCH TO CELLULOSE

The procedure for these experiments has been based on work by L. B. Hallows, not yet fully described. The dyes were Durindone Blue 4BC (C.I. Vat Blue 5), representing the indigo series, and Caledon Jade Green XN (C.I. Vat Green 1), representing the anthraquinone series. Among experimental features of the work were the following— (i) purified dye was ground in water without dispersing or suspending agents for a standard time; (ii) different proportions of potassium carbonate and sodium formaldehyde-sulphoxylate (Formosul) (C.I. Reducing Agent 2) were employed; (iii) in some experiments the oxygen present in the steam was removed by including alkali and Formosul in the steam generator; (iv) the starch layer tended to liquefy in steam because of its high electrolyte content, and the specimen was therefore held horizontally in the steamer; (v) the dye was immediately reoxidised at the end of the steaming time to arrest further migration; and (vi) light was excluded during the steaming.

Durindone Blue 4BC

(*C.I. Vat Blue 5*)

Including a short initial reduction period, during which there is little transfer of dye in experiments in which the proportion of reducing agent is diminished, dye transfer is analogous to that of a direct dye. The transfer characteristics in these circumstances are as follows—

LOW-ALKALI CONDITIONS, air removed (0·25 g. potassium carbonate, 0·5 g. Formosul, and 0·25 g. dye to each 10 g. starch plus 250 mg. dye)— Equilibrium exhaustion 61% in 150 min.; half-exhaustion time 47 min.; time of half-penetration (diffusing front not sharply defined) approx. 20 min.

HIGH-ALKALI CONDITIONS, air not deliberately removed (10 g. potassium carbonate, 5 g. Formosul, and 0·25 g. dye to each 10 g. starch)— Equilibrium exhaustion 87% in 180 min.; half-exhaustion time 46 min.; time of half-penetration (diffusing front sharply defined) approx. 18 min.

The appearance of the sections in these two experiments was very different (Fig. 5). In the low-alkali series the dye in the starch was in the form of large, discrete flakes and remained so during prolonged steaming. The dye in the high-alkali experiments was much more completely dispersed, giving a deep colour to the starch layer, and the visible dye particles were much smaller.

It seems as though, in the first series, only a small proportion of the leuco compound in the starch was soluble at any one time, and dye was transferred from a comparatively dilute solution, maintained at a more or less constant concentration by progressive dissolution of leuco compound. With the high-alkali series, transfer must have occurred from much higher concentrations of leuco compound in the starch.

Two factors were probably responsible for the difference. Firstly, the excess of alkali in the one encouraged solubility in any case. Secondly, the larger proportion of electrolyte induced a much greater deliquescence and so, in the high-alkali series, the starch during steaming was much more swollen with water than in the corresponding low-alkali series. This is not reflected in the cross-sections because the specimens had to be dried before mounting. Nevertheless, this swelling of the starch called for great care in getting the specimens into a suitable condition for mounting, without causing damage. With these differences, it is surprising that the speed of the diffusing front through the cellulose film is almost identical in the two series, although the amount of dye transferred is different.

There is evidence in the high-alkali series of some local denudation of the starch layer near the interphase boundary. In the low-alkali series it is possible to detect migration of dye in the starch towards the outer surface after long steaming.

Caledon Jade Green XN

(*C.I. Vat Green 1*)

The general results with this dye follow those obtained with the blue dye. Two series of experiments were again carried out, under the same conditions as before except that in the high-alkali series the weight of potassium carbonate was reduced to 5 g. The differences in transfer behaviour between the two series are striking— equilibrium exhaustion 84·5% in 180 min. (high alkali) and 21% in 120 min. (low alkali); half-equilibrium time 16 and 18 min.; half-penetration time 20 and 30 min., both with sharp diffusion fronts, that in the high-alkali series being markedly so. Again there is the distinction between a fine granular deposit of dye in the starch of the high-alkali series and a coarsely granular one in the low-alkali series (Fig. 6). There is some evidence of local denudation in the former series.

In experiments with both vat dyes, there was a common feature not represented very clearly in the photographs, viz. the formation of colourless crystals (presumably from the added electrolyte) on the free surface of the Cellophane.

DISPERSE DYES BETWEEN STARCH AND SECONDARY CELLULOSE ACETATE

Duranol Red 2B

(*C.I. Disperse Red 15*)

This system appears, among all other systems examined, to represent a simple transfer, relatively unaffected by secondary factors. It should be pointed out that, apart from the presence of thickener itself, there was no auxiliary product to assist dispersion or to stabilise the suspended dye, which was purified and, after recrystallisation, ground in a ball-mill, with distilled water only, for 24 hr. The establishment of equilibrium conditions is unambiguous at an exhaustion of 91% in 120 min. Half-exhaustion is at 22 min. steaming if the 10% of dye transferred during the drying-down of the starch is included; the time of half-penetration (see below) is approx. 15 min. Following are the principal features revealed by cross-sections of the system—

(*a*) Discrete dye particles, roughly uniform in size, are present in the starch layer (Fig. 7). These tend to grow in size somewhat and diminish in number in the early stages of steaming. Later, as substantial proportions of dye are transferred to the cellulose acetate, they get smaller and fewer. The particles themselves are dark, and are not bright red like the dye in its highly dispersed forms. In the starch there is a continuous faint background of red; in the cellulose acetate the dye appears to be completely dispersed. This series is a pictorial demonstration of the normally accepted mechanism for the dyeing of hydrophobic fibres with disperse dyes, viz. from a bath maintained at saturation by an excess of the solid form.

(*b*) During the drying-down of the paste, some dye migrates to the cellulose acetate. It is about 10% of the total dye, and although migration occurs in the cold, dye is seen to penetrate, albeit at low concentration, almost half-way through the cellulose acetate film. In the main transfer, during steaming, the front of the diffusing dye is relatively sharply defined. As might, perhaps, be expected when transfer depends on a two-stage mechanism of dissolution and migration, there was no evidence of uneven concentration of dye within the starch,

i.e. denudation of the region next to the fibre phase, at any time during the steaming. There is, indeed, strong evidence that fully dispersed dye can diffuse very rapidly in the starch.

The general picture given above is supported by the results of desorption experiments, in which dye is first transferred from starch to cellulose acetate by prolonged steaming. The starch is then removed, replaced by a fresh layer containing no dye, and the whole steamed together. Equilibrium is reached in under 60 min. with a desorption of 5·7% of dye. For all times of steaming there is no diffusion front in the starch, the colour first showing itself and then deepening uniformly throughout the starch layer as steaming continues. No separation of solid dye was observed.

MIGRATION OF SOLUBLE DYES FOR CELLULOSE ACETATE BETWEEN STARCH AND SECONDARY CELLULOSE ACETATE

Solacet Fast Scarlet B
(C.I. Acid Red 53)

There are some unusual features of dye transfer with this system, in that exhaustion from starch is low (under 10%), migration relatively slow, and equilibrium never attained. As discussed earlier by Daruwalla [8], there is an unusual relation between the original concentration of dye in the starch and the exhaustion after a given time of steaming, the higher the concentration the higher the exhaustion. This, from previous experience with acid dyes, seems to be a criterion of low affinity. A preliminary reversal of migration arising from the same cause is also observed. Dye transfer corresponding to about 75% of the maximum attainable by prolonged steaming occurs on drying-down the paste at room temperature. In the first hour of steaming considerable migration back to starch occurs, and then the transfer to cellulose acetate recommences. It is interesting to follow what happens from the cross-sections (Fig. 8)—

(*a*) There is evidence of the limited solubility of the dye, and at high concentrations (0·08 mg. dye per standard area) there are no solid deposits. Evidence of slight heterogeneity in the cellulose acetate is due rather to delustring than to irregularity in the distribution of dye. It is more in evidence in systems where an electrolyte is present in the starch and the water content of the system in steam is higher.

(*b*) From the cross-sections it is seen that the relatively heavy strike occurring as the paste is dried down on the cellulose acetate at room temperature corresponds to very imperfect penetration. On steaming, little diffusion is observed for some 90 min., and dye has only penetrated half-way into the cellulose acetate in 240 min. This slow forward movement was found in other experiments with dyes of this class (see below). Although not readily demonstrated in monochrome photographs, the return of dye from cellulose acetate to starch is seen by direct inspection when the total dye content of the system is low.

Solacet Fast Scarlet B and Sodium Chloride

To a system similar to the previous one was made an initial addition of sodium chloride twenty times the weight of dye in the paste. This increased the exhaustion both on drying-down and on steaming, though not to high values (without salt— drying-down 4·9%, 480 min. steaming 8·5%; with salt— drying-down 12·5%, 480 min. steaming 17·7%). Compared with the former system the most noticeable difference is that the dye in the starch phase appears to be much better dispersed, and large discrete particles appear only after prolonged steaming. This greater uniformity is not, apparently, a consequence of the deliquescent action of salt, since it is found in the starch layer even when there has been no steaming. Although exhaustion is higher, here, again, diffusion into the cellulose acetate film is slow. Even after 480 min. steaming the diffusing dye has not reached the outer face in quantity.

Solacet Fast Scarlet B with Sodium Thiocyanate

The presence of this swelling agent (133 times the weight of dye) causes many changes in the behaviour of the system, although it is certain that they are not fully represented in the cross-sections because, as mentioned earlier, these must be dried before embedding. Thus, in none of the sections does any evidence remain that the cellulose acetate has been swollen, although there has certainly been irreversible swelling of the starch. The starch has again a grain structure, although it is not filled with large particles of dye. The exhaustion is now of the order of 40% at 120 min., the initial value on drying-down being 13%. In these experiments there is no reverse migration at the commencement of steaming. One of the most interesting observations is that, although exhaustion is increased very materially by the thiocyanate, rate of penetration of dye is not, and at the end of 240 min. the dye has gone only three-quarters of the way through the cellulose acetate film. The diffusion front is not so sharply defined as with the disperse dye.

Comparison of the course of penetration of Solacet Fast Scarlet B into cellulose acetate with that of Chlorazol Sky Blue FF into cellulose is instructive. With both systems penetration is relatively slow. With the Solacet dye the diffusion front is not very sharply defined, especially after long steaming, and this situation does not appear to be changed when the total exhaustion (intrinsically low) is increased by assistants. With the direct dye the front is sharp. Thus, it seems that a similar result is being produced by two different causes— the physical difficulty of movement of hydrated dye particles in a hydrophobic fibre on the one hand, and the slowing down of intrinsically diffusible dye molecules by sorptive forces on the other.

ACID DYES BETWEEN STARCH AND CELLULOSE
Coomassie Brilliant Blue FF
(C.I. Acid Blue 15)

Curiosity was felt about the local details of the migration of some of the acid dyes, since the

partition between the two phases is unusual with some members of the class. With Coomassie Brilliant Blue FF (C.I. Acid Blue 15), for instance, the dye transferred to cellulose has been shown to pass through a maximum as steaming continues. Evidence of back diffusion during part of the time naturally aroused the hope that this phenomenon could be observed directly. The partition data for transfer from an originally dry thickener film to cellulose on steaming conformed to the pattern first discovered by Patel[2], maximum exhaustion of about 40% being reached in 60 min., and the exhaustion then falling steadily to about 26% in 240 min. Dye penetration, with the front diffuse, was rapid, corresponding to halfway penetration in 7 min., and the dye reaching the outer face of the cellulose in substantial concentration in about 17 min., but not becoming uniformly distributed until after 40 min. It has not been easy to show in monochrome (although colour photographs, which are more effective, are available) the reverse passage of dye from the cellulose to the starch after the maximum has been passed. However, this can in fact be seen directly on comparing specimens taken after 120 min. with those taken after 180 min. steaming, the starch having become more or less uniformly darker and the cellulose uniformly lighter after the longer steaming.

There is, however, evidence after steaming for 60 min. and longer that there is some tendency for dye to become less concentrated in the starch immediately contiguous to the interphase boundary (Fig. 9). With a dye which diffuses so rapidly in both phases and has so low a true affinity for cellulose it is unlikely that this effect is due to a migration of dye into the cellulose more rapidly than it can be replenished by diffusion from the body of the starch. The following mechanism is the more likely. After about 60 min. steaming a temporary equilibrium may be established between the concentration of dye uniformly distributed in the starch phase and that similarly distributed in the cellulose phase. However, recent work by Parikh in this laboratory has shown that an isolated starch film maintained in steam will go on steadily increasing in weight until it gets so soft that it falls off the suspending hook. This would, in turn, suggest that the next movement of dye in the printing system would be towards the free surface of the starch, where the main uptake of water is taking place. Previous evidence has led us to expect that dye will diffuse back from the cellulose to the starch less readily than it diffuses within the highly swollen starch; hence the impoverishment of the inner region.

In all this work, with a dye more mobile in the fibre phase than any examined hitherto, there is an increased danger that migration, in one direction or other, may take place after the samples are removed from the steamer and prepared for sectioning. This much reassurance can be given, that specimens removed from the steam, embedded, cooled rapidly in ice (30 min.), cut, and mounted were identical with those which were kept embedded for 24 hr. before cutting.

Two-colour Effects

An interesting observation with Coomassie Brilliant Blue FF is that, while the dye in the starch phase is a uniform brilliant blue, that in the cellulose appears to consist of two fractions— a rapidly diffusing one which shows as an extended red fringe in front of the main, slowly moving bluish diffusion front.

The original dye had been purified by crystallisation. It was now chromatographed on alumina with 95% ethanol. There were initially two fractions— a small strongly adsorbed reddish-blue one and a large lightly adsorbed clear blue one. The order was reversed on filter paper, suggesting that the reddish one was more acid in properties than the blue. After three chromatographic separations the red component seemed to be removed, and the blue product was regarded as pure. This fraction was incorporated in a printing paste, and transfer experiments to cellulose performed in the usual way.

The following observations were made—

(1) Exhaustion to cellulose is lower with the chromatographed dye than with the original.

(2) The two-colour effect persists, with this difference, that for steaming times up to 60 min. the dye in the starch layer is again blue, but that in the cellulose is wholly red. After long steaming times the dyed cellulose is again bluer. There is thus either a tautomeric change influenced by the environment of the dye, an irreversible chemical change induced by heat, or some radical difference in the state of aggregation in the two media. This phenomenon was not examined further, but might prove interesting on closer investigation.

Coomassie Brilliant Blue FF dried on

The dye is very mobile in both starch and cellulose, and Patel[2] has shown that it can be transferred in substantial proportions in the cold when a layer of print paste is applied to cellulose film and dried at room temperature. An exhaustion of 30% was obtained in the present experiments, and when the system was later steamed the exhaustion, after some irregularities, slowly diminished, i.e. dye returned to the starch. From the cross-sections it was seen that dye had penetrated through the cellulose layer merely on drying, although the concentration was not uniform but greater in the cellulose near the interphase boundary. The concentration of dye in the starch was less near the boundary than elsewhere. Steaming for 180 min. was required to make the dye distribution uniform in each phase. The two-colour effect occurred here also.

Coomassie Brilliant Blue FF with Urea

Urea is used either as a dispersing medium for some acid dyes or as a swelling agent for the cellulose in industrial printing styles. The presence of urea in the starch film along with the dye has the following effects—

(1) The total exhaustion to cellulose at any time during steaming is diminished, being the less the greater the proportion of urea.

(2) Maximum exhaustion occurs earlier (25 min. instead of 60 min.).

(3) Penetration of the cellulose film is more rapid, uniform dyeing through the thickness of the film being established in about 20 min. instead of 60 min.

(4) After 60 min. dye appears to recede from the side of the cellulose film in contact with steam and move towards the starch. At the same time dye moves toward the free side of the starch layer away from the cellulose. As this movement is greater in starch than the corresponding one in cellulose, the starch layer becomes visibly denuded, a thin layer near the interphase boundary being left practically colourless.

(5) The two-colour effect is observed. In forward diffusion from starch to cellulose, the red component diffuses more quickly. In reverse movements the blue component seems to recede, leaving the cellulose coloured faintly reddish blue. This evidence of a preferential attraction of the red component for cellulose may be connected with an original observation of Patel [2], who found, from a partition isotherm drawn for the values of maximum exhaustion with different proportions of dye in the system, that there appeared to be a small number of basic groups in the cellulose leading to stronger fixation of a corresponding number of molecules of acid dye. Since, from alumina chromatography, the red fraction seems to be the more acid, it may be responsible for the effect observed by Patel.

PROTECTION OF THE STARCH— From the explanation suggested above, the secondary migration effects may be caused by water being taken up from steam more readily by starch than by cellulose. It follows that these effects would be suppressed if direct access to steam were denied to the starch layer. Steaming was therefore carried out with a starch–cellulose system in which a thin cover-glass was stuck on to the outer face of the starch. Denial of water in this way had the following effects—

(1) Initial migration of dye to cellulose is slowed down.

(2) Maximum value for exhaustion on cellulose is diminished.

(3) Return of dye from the cellulose to the starch is much delayed (from 60 to 120 min. steaming time).

(4) Denudation of the starch layer at the region near the interphase boundary is much delayed and the visible effect much less pronounced.

These results, therefore, are very much as expected.

Naphthalene Red EA
(C.I. Acid Red 13)

This dye is very soluble and diffuses much more rapidly than Coomassie Brilliant Blue FF. The partition behaviour of this kind of dye is distinctive in that exhaustion to cellulose increases very rapidly, passes through a sharp maximum (at 10 min. steaming time, 26% exhaustion), falls slightly, and then remains constant for steaming times up to 180–240 min. The course of dye migration, as seen from cross-sections (Fig. 10), is as follows—

(1) The dye is so mobile that some migrates to the cellulose while the dye-containing starch film is being attached to it.

(2) Complete penetration of the cellulose film occurs after steaming for 5 min., and uniform distribution in the film after 10 min.

(3) Migration of dye in the starch away from the interface is very pronounced as steaming continues, and denudation is marked. This denuded layer tends to fill up again after steaming for 120 min.

Naphthalene Red EA dried on

Drying-on the printing paste results in full transfer occurring at room temperature, and steaming causes reverse migration. Penetration through the complete thickness is brought about by drying alone, but dye is not evenly distributed through the layer until after 20 min. steaming. After 40 min. a receding diffusion wave commences in the cellulose, with dye beginning to concentrate near the interphase boundary, and after 180 min. the cellulose is pink only. This corresponds to a fall in the exhaustion from 30% to 17%.

Naphthalene Red EA and Coomassie Brilliant Blue FF together

Both of these dyes show reverse migration, each having a maximum exhaustion, but that for the red dye occurs after 10 min. steaming, that for the blue after approx. 60 min. If the occurrence of a maximum is to be ascribed only to the relative water uptakes of starch and cellulose from steam, it is surprising that the maxima for the two dyes do not occur at the same time. To investigate this point steaming experiments were performed with a starch film containing a mixture of the two dyes. By the use of suitable filters, it was possible both to estimate the partition of each dye in presence of the other and also to examine their individual progress in the cross-sections. This work has been extended by J. F. Dastur, and it is hoped later to give a separate account of it. In general, it can be said that each dye preserves the migration properties which it showed when examined by itself, the maximum exhaustion occurring at the characteristic time of steaming, forward and reverse progress of dye in the two phases as revealed in the cross-sections also being very similar. At any given time, the exhaustion of either dye was enhanced a little by the presence of the other.

It may be useful to record that, in the absence of monochromating apparatus which would supply light of sufficient intensity to allow absorptiometry or photography of the sections to be performed in a reasonable time, or of standard light filters which were sufficiently discriminating without unduly attenuating the light, satisfactory results were ultimately attained by using filters of Cellophane dyed with the respective dyes.

CHROME MORDANT DYES BETWEEN STARCH AND CELLULOSE

Two mordant dyes— Solochrome Red B and Azol Printing Red R extra (C.I. Mordant Reds 9 and

66)— have been investigated by W. K. Birtwistle and E. Walker, and it is hoped also to give a full account of their work later. Again speaking in general terms, the dyes in the absence of chromium salts behave similarly to Naphthalene Red EA, i.e. as very soluble, rapidly diffusing acid dyes. In the presence of chromium acetate, a smaller proportion of dye diffuses rapidly into the cellulose, leaving the starch heavily and uniformly coloured (Fig. 11). The distribution of dye established in 5 min. is not substantially changed after steaming for 60 min. As other work established, an experiment performed under these conditions results in rapid insolubilisation of dye in the starch layer, leaving only a fraction of the original dye mobile.

Quantitative Estimation of Dye Diffusion

PROCEDURE

An outline of the apparatus used has already been given. It should be emphasised that, at this stage, the homogeneity, structural and optical, of the starch layer was sufficiently doubtful to cause the layer of fibre-substance only to be examined. Further, since a relatively short time was available for the work, it was decided to concentrate on the direct dye Chlorazol Sky Blue FF (C.I. Direct Blue 1) and its migration into cellulose.

A projection of the cross-section which would allow good definition could not much exceed a width of 15 mm., and the possible thickness of the cross-sections themselves was limited. This required the image to be scanned through a very narrow slit (0·015 mm. or less), calling therefore for a very sensitive photomultiplier. It was decided finally that the image projected by the microscope should be scanned directly and not as a photographic transparency.

CALIBRATION

Various suggestions for calibration were considered. One, which might be capable of development later for very accurate work, was as follows. Sheets of Cellophane were dyed to different known dye contents and assembled into a pack in correct order, and a cross-section of the assembly was taken to form a small step-wedge which could be mounted alongside each specimen for examination. As also the construction of comparison and split-beam photomicrometers would have required too long a time, it was finally decided to rely on the essential stability of the instrument and to prepare a calibration curve using cross-sections of a number of Cellophane films, each of which had been steamed for 300 min. in contact with starch film containing dye until the dye was evenly distributed through it. The dye content of part of this film was determined by extraction with 20% pyridine, and the concentration of the extract determined colorimetrically. Making certain corrections for the difference between the dimensions of the film in steam and when dry, the ultimate readings of the photomultiplier could thus be expressed in terms of local dye concentration as grams per litre.

OPERATION OF PHOTOMULTIPLIER

It is not proposed to discuss the characteristics or operation of this instrument in great detail. A good deal of work was first required to reduce the dark current in the tube to acceptable limits and to select from available tubes that with the greatest stability and the highest gain. Under the best conditions, however, the dark current occupied most of the most sensitive range (10^1) and an appreciable part of the next (10^2). The 10^3 and 10^4 sensitivity ranges were found to be appropriate for most of the present work. They were nominal only, and the meter reading was not linearly related to the photomultiplier current for low readings.

SCANNING THE IMAGE

The operating head of the lead screw, already described, which traversed the photomultiplier tube in its light-tight case with slit across the projected image, was graduated in sectors of 22·5°, and rotation through this angle moved the detector 0·0061 cm. This allowed 70 readings to be taken across the image of a representative cross-section. Following is a brief summary of experimental points taken account of during the preparation and scanning of specimens—

(1) To keep all readings within one sensitivity range of the instrument, the intensity of the illuminating light must be modified as required by the use of Chance neutral filters, each of which has a known transmission.

(2) Internal reflection effects must be eliminated by using the correct mountant, in this case Canada balsam.

(3) Presence of the starch layer also can interfere with the measurements, and it is better removed before cross-sections of the Cellophane are made.

(4) It is very difficult to obtain strictly uniform field illumination or to avoid some irregularities apparently due to imperfections in the layer of mountant. Therefore, after scanning the image of the specimen, the slide was displaced so that this image was just out of range of the detector, and then moved back over the same distance taking the same number of readings through the blank slide, making allowance for lead-screw backlash. The second set of readings were ground or control values, to be subtracted from the corresponding readings for the image.

(5) It was very desirable to find the correct concentration of dye, originally in the starch paste, necessary to produce cellulose specimens after steaming in which the range of dye concentration set up could be measured by using one sensitivity range of the photomultiplier only (preferably 10^3).

Fig. 12 shows the curve relating corrected photometer readings with distance x across the section for a cellulose film steamed for 60 min. in contact with the dye-containing starch film, and Fig. 13 examples of the concentration–distance relation after different times of steaming. In these curves, the first few readings, taken as the slit passed from clear slide into the section, have been neglected, since a number of distracting effects are encountered; i.e. $x = 0$ is thus represented by a point 1–2 mm. within the boundary of the image. Likewise, with long steaming times, when the dye
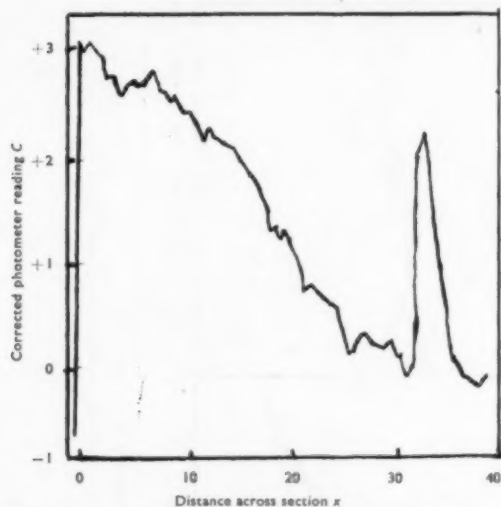
FIG. 12— Example of Photometric Determination: Cross-section of cellulose containing Chlorazol Sky Blue FF after steaming for 60 min.

x = Distance from surface of contact with starch
$C = I_b - I_s$ photometer units corrected for base reading

has penetrated to the outer face of the Cellophane, the last reading is neglected, being subject to similar interferences.

The following observations, which are not brought out by direct visual inspection, are significant—

(1) The curves start from lower and lower dye concentrations near the interface as steaming proceeds. Previous concentration–distance curves for finite baths have tended to show that the strike concentration remains substantially unchanged as dyeing proceeds. The present experimental evidence does not rigidly exclude this possibility if the "constant-concentration layer" is conceived as being extremely thin, but this would imply a very high concentration gradient in the outer layer for the longer steaming periods.

(2) Special features distinguish the present system from almost any laboratory dyeing system, since the bath is very small in volume and represents an extreme example of the "finite" condition.

(3) There is a viscous "dyebath" with no stirring possible, so that intensely localised exhaustion of the "bath"— inversion of the strike — can occur near the surface of the cellulose.

In these circumstances it is reasonably probable that the treatments for the normal "finite" bath would be inappropriate.

(4) The increased scatter of experimental points in systems that have been steamed for more than 1 hr. occurs on repetition and must be regarded as a real effect. It may denote an influence of prolonged steaming on the homogeneity of the cellulose film, incipient crystallisation of the dye, or some similar effect.

ANALYSIS OF THE RESULTS

Although the results expressed in Fig. 13 must be subject to the criticism that the whole experimental technique requires further development, an attempt has been made to assess the significance of the results in comparison with notable efforts that have already been made to determine the relation between local dye concentration C and diffusion coefficient D.

From a comparison of successive curves (Fig. 13) it is possible to determine graphically the rate of diffusion dS/dt at any point x within the film, and from any one curve the concentration gradient dC/dt and ambient concentration C at that point can be measured. It will be noted that graphical estimation of dS/dt and dC/dt gives a twofold source of reading error, especially when the slopes of the curves are acute. Direct substitution into the equation for Fick's law is now possible [9]—

$$\frac{dS}{dt} = -DA\frac{dC}{dx}$$

An alternative development, due to Crank [10], expresses the diffusion equation as—

$$D = -\frac{1}{2t}\frac{dx}{dC}\int_0^C x\,dC$$

where the definite integral is the area under the curve below the ordinate for C corresponding to a given value of x.

Graphical substitution can be applied here also. This treatment is subject to two limitations— (a) that D may vary only with C and not with x or t independently of C, and (b) that the conditions shall represent the diffusion of dye into an infinite solid.

The latter condition is reasonably fulfilled for all specimens in which penetration has not gone beyond three-quarters of the thickness of the film, since entrance of dye is on one side only.

The relations between C and D given by the two methods are shown by the array of points in Fig. 14. The relation between C and D determined by the Crank method for the dyeing experiments of Neale and Garvie [8] was linear. From the present results there are indications by both methods of a relatively constant value for D, almost independent of concentration where the general concentration is low, i.e. in the interior of the film. Near the boundary with the starch D rises sharply with C, which points either to a different diffusion mechanism when the cellulose is closer to saturation or to structural differences in the cellulose itself between the central and the superficial regions of the film, differences which have, of course, been frequently demonstrated.

Explicit conclusions at this stage of the work must be regarded with the greatest possible reserve. More as a report of progress than anything else, the summary in Table I compares the results of different workers on the relation between diffusion coefficient and local concentration of dye. It should be pointed out that, with the exception of the work of Neale and Garvie [8], almost every attempt to deduce this relation has been based upon measurement of partition between the whole of the dyebath phase and the whole of the fibre
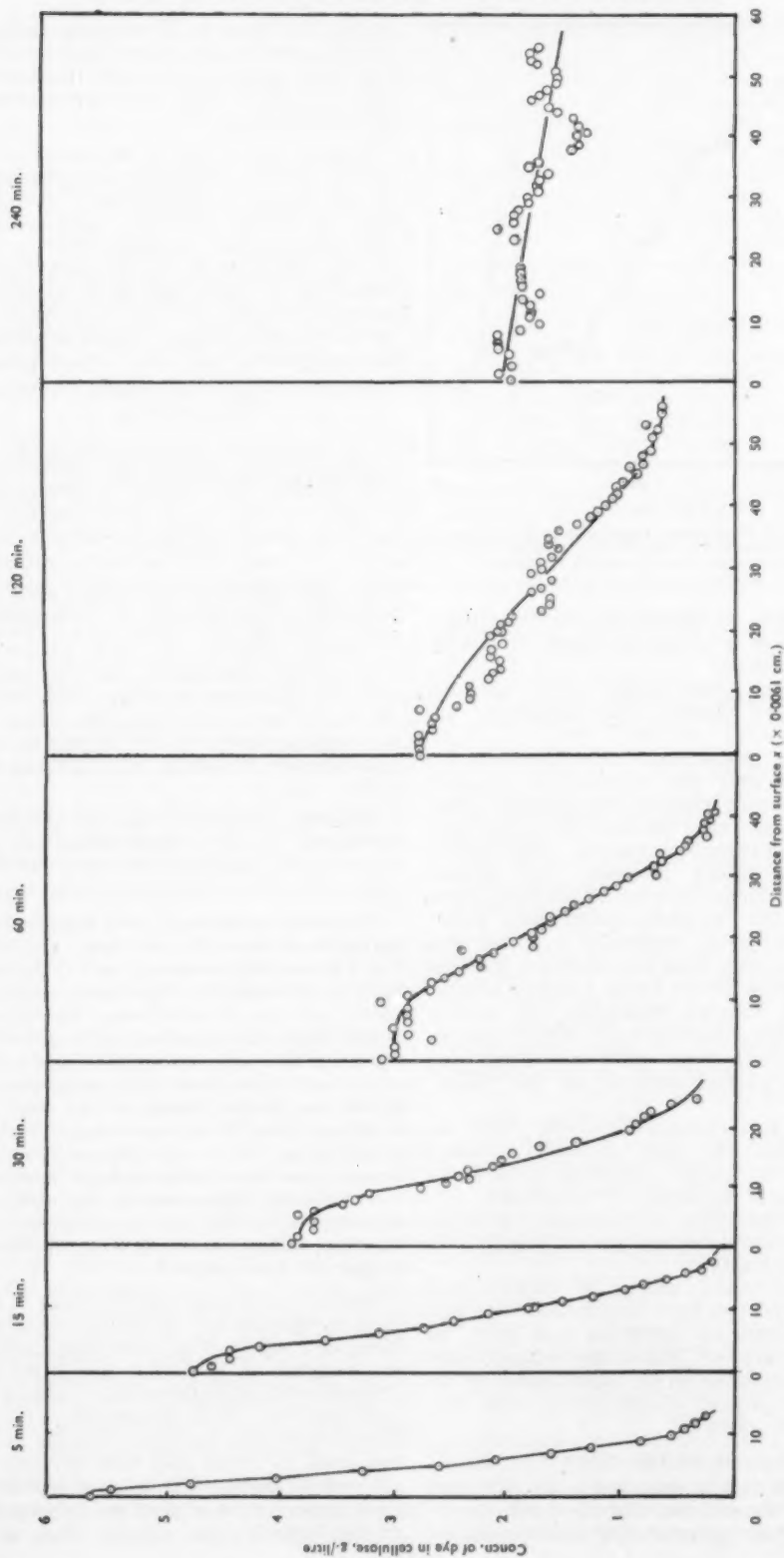
Fig. 13— Distribution of Chlorazol Sky Blue FF in Cellulose after Different Times of Steaming
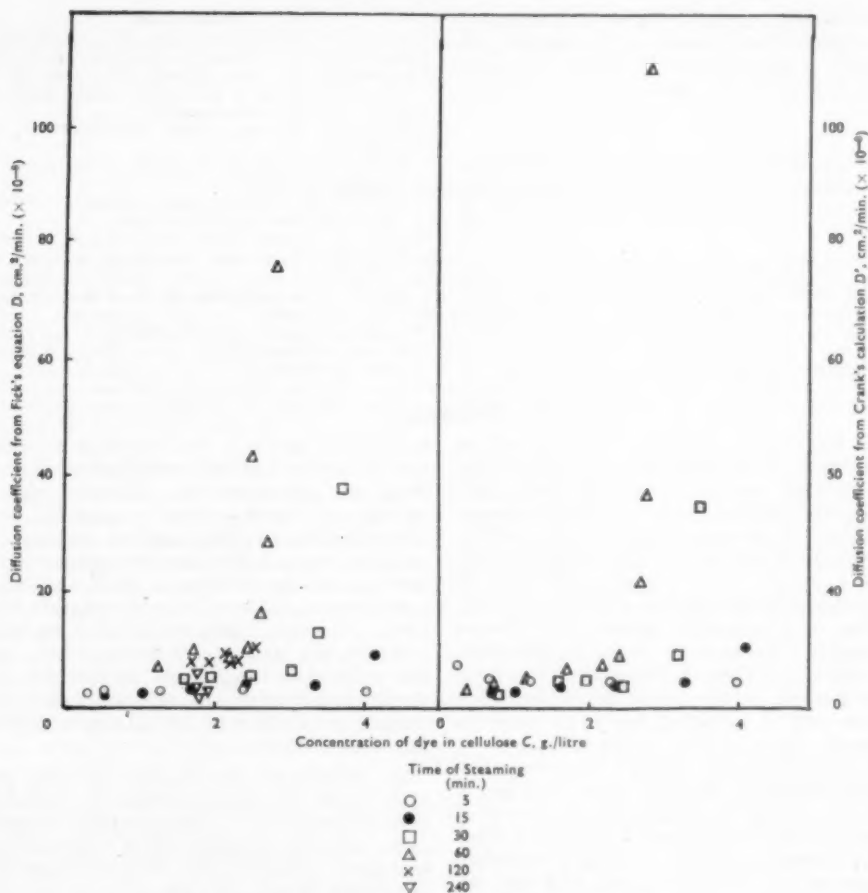
Fig. 14— Relation between Diffusion Coefficient and Concentration

TABLE I

Workers	Garvie and Neale[9]	Crank[10]	Myers[1]		Present Work	
Conditions ...	Block of Cellophane sheets in dyebath	Experimental data of Garvie and Neale[9]	Printing systems		Printing systems	
			Munshi's results[5] (H_2O content not constant)	Myer's results[1] (constant H_2O content)	Neale's calculation	Crank's calculation
Range of dye concn., g./litre	0–20	0–20	3–8	4–14	0–5	0–5
Range of diffusion coefficient, cm.^{2}/mm. ($\times 10^{-8}$)	5–25	5–25	0–72	0–96	2–73	3–107
Relation between D and C	$D_C = D_0 C^{\frac{1}{4}}$	$D_C = 418(1+2\cdot4C)$	Minimum at 5 g./litre	Minimum at 9 g./litre	D increases with C, at first slowly, then rapidly	
Additional features	Wide scatter in D–C plot	Fairly strict linear relation	—	—	Indications of minimum at 1 g./litre by Crank's calculation. D seems to depend on both x and t	

phase. The present appears to be the first attempt, even as a preliminary attack on the subject, to make direct measurements of local dye concentration in a printing system.

*   *   *

We are indebted to the Courtaulds Scientific and Educational Trust Fund for a scholarship which enabled one of us (H.B.H.) to take part in this work.

DEPARTMENT OF TEXTILE CHEMISTRY
COLLEGE OF SCIENCE AND TECHNOLOGY
UNIVERSITY OF MANCHESTER

(*MS. received 20th July 1957*)

References

[1] Myers, G. D., and Turner, H. A., J.S.D.C., **69**, 648 (1953).
[2] Patel, R. B., and Turner, H. A., *ibid.*, **68**, 77 (1952).
[3] Vickerstaff, T., *The Physical Chemistry of Dyeing* (London: Oliver & Boyd. 2nd edition 1954), p. 6.
[4] Möller, Private communication.
[5] Munshi, R. H., and Turner, H. A., J.S.D.C., **65**, 434 (1949).
[6] Florida, C. D., and Davey, C. N., *J. Sci. Instr.*, **30**, 409 (1953); A.E.R.E. Specification 304, Catalogue 3–7/5104 and 3–7/0270, Drawing No. D 23190.
[7] Reilly, D. A., and Turner, H. A., J.S.D.C., **67**, 103 (1951).
[8] Daruwalla, E. R., and Turner, H. A., *ibid.*, **69**, 240 (1953).
[9] Garvie, W. M., and Neale, S. M., *Trans. Faraday Soc.*, **34**, 335 (1938).
[10] Crank, J., J.S.D.C., **62**, 372 (1946).
[11] Patterson, D., and Ward, I. M., *Trans. Faraday Soc.*, **53**, 1516 (1957).

Discussion

Dr. D. PATTERSON: One of the difficulties associated with microdensitometers, caused by variations in light intensity across the field of the microscope, can be eliminated in a simple manner by moving the object being scanned instead of the photomultiplier and slit. In this method [11] the latter are kept fixed, and a mechanical drive is applied to one of the movements on the mechanical stage of the microscope. In measurements of the optical density, and thus the dye concentration, at any point in the fibre, the value of I_0, the light intensity incident on the specimen, is the same throughout, and no correction has to be made to the measured values of transmitted intensity.

Mr. TURNER: We agree with Dr. Patterson, but again call attention to the fact, made clear in the text, that we were making a preliminary survey of the problem, with very little time, and with apparatus which could not be quickly modified. Our procedure is a reflection of the fact that we could get more accurate scanning of the cross-section, in terms of the value x for each reading, by traversing the detector than by using the mechanical stage of the microscope to move the object. It will be seen that we did compensate for irregularities in the field, although not necessarily for those in the mounting of the cross-section, by control experiments. Further work in the Department is being done with an autographic apparatus in which the object is moved by an accurate reduction gear from the mechanism which displaces the chart along the x axis.

Dr. E. ATHERTON: A series of curves are presented in this paper, showing the relation between concentration of dye, distance within the cellulose sheet, and time. The experimental points depart from the best mean curve to an increasing extent as diffusion proceeds, and the authors state that this departure and in fact this general pattern of behaviour are repeatable. If one considers dye transfer as arising from sequential reactions (diffusion through print paste and diffusion through cellulose), it is not difficult to imagine an oscillatory condition at the cellulose surface, in which high exhaustion is followed by replenishment from the body of the paste. This would lead to an oscillatory rather than a smooth penetration curve, which in fact is found by the authors. It should be possible to calculate the diffusion coefficient of the dye from the rate of migration of any maximum or minimum into the cellulose.

Mr. TURNER: To some extent this question answers Dr. Patterson, in that Dr. Atherton has detected from our unrefined efforts a very interesting and very plausible effect. We owe him our thanks for pointing it out. There is no doubt in my mind that the sequence does occur, although we have been trying, with none too consistent results, to show it by demonstrating gross local exhaustion in the thickener layer. Could the same effect be obtained in a system in which the medium was moving in a mean direction opposite to the direction in which the dye diffused? We think it very likely that water can move from the free side of the Cellophane towards the starch during steaming.

Somewhat light-heartedly, it may be suggested that we are seeing the end of the dyemaking industry as it exists at present. Birds and fish owe some of their colours to interference effects. Have we here a kind of Lipmann effect, which, if developed, would do away with many of the complicated organic compounds now used for coloration?

The Colouring of Vinylon

S. NOMURA and K. TANABE

Vinylon is usually made by spinning an aqueous solution of polyvinyl alcohol, heat-treating the water-soluble fibres obtained, and subsequently acetalising with formaldehyde. As both hydroxyl and acetal groups in the accessible region are concerned in the dyeing of vinylon, it is generally intermediate in dyeing behaviour between cellulosic fibres and typical synthetic fibres. The dyeing properties of vinylon with direct dyes are thus affected not only by crystallisation due to heat-treatment and degree of acetalisation but also by the acetalising conditions.

For the practical dyeing of vinylon to medium or heavy depths direct, sulphur, vat, azoic, disperse, and metal-complex dyes may be employed, and their fastness is not greatly different from their corresponding fastness on other fibres. Dope dyeing is now most advantageous for blacks and dark blues, and is carried out on a commercial scale.

I— Introduction

With the advance of knowledge of high polymers and fibre structure in the last thirty years, a number of man-made fibres have been developed. Each of them possesses not only mechanical properties required for textile uses, but also characteristics of its own. However, as far as dyeing properties are concerned many of them fall short of satisfaction for apparel uses. In the meantime, as their commercial production has increased, the dyeing of man-made fibres, particularly that of synthetic fibres, has been investigated as a matter of pressing necessity. As solutions to this problem, high-temperature dyeing, carrier dyeing, and other special dyeing methods have been devised along with the developments of various dyes for synthetic fibres. In some cases, modification of the fibre itself by the introduction of dye-receptive groups, e.g. by copolymerisation, polymer blending, or chemical treatment, and also dope-dyeing are being carried out or are under consideration.

In this respect, vinylon is no exception, but the situation is somewhat different. Vinylon is less hydrophobic than the so-called typical synthetic fibres, and is by no means difficult to dye, for it may be dyed to medium depths with most groups of dyes. Deep colours, however, can be obtained on vinylon with satisfactory brightness and fastness only with a limited number of groups of dyes. This fact seems to account for the practical difficulties of vinylon dyeing, and it is desirable that suitable dyes for vinylon should be found to fulfil these requirements.

II— Relation between Dyeability and Fibre Structure

1. MANUFACTURE AND PROPERTIES OF VINYLON

Polyvinyl alcohol was discovered by W. O Herrmann and W. Haehnel[1] in Germany, and they produced polyvinyl alcohol fibre for the first time[2], but the product had insufficient wet-heat resistance for apparel uses. So attempts were made to obtain from water-soluble polyvinyl alcohol a fibre which is suitable for apparel uses with adequate dry- and wet-heat resistance, i.e. a fibre

which shows no appreciable shrinkage in hot water, especially boiling water, and such has met with success in Japan[3]. The fibre was named *vinylon* in 1948, and production is being carried out on a commercial scale (annual production in 1956: 23,635,000 lb.).

The processes of manufacture of vinylon as now marketed and the significance of each process are shown in Table I. The general properties of formalised vinylon and benzalised vinylon are given in Table II.
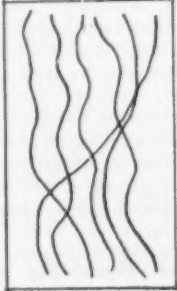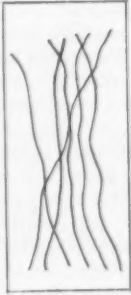
TABLE II
Properties of Vinylon

Property	Formalised Tow (bright, high-tenacity)	Formalised Staple (dull, crimped)	Benzalised Staple (dope-dyed)
Denier	1·3	1·4–3·0	3·0
Dry tenacity, g./denier ...	6·4–7·0	4·2–5·7	4·0–4·5
Wet tenacity, g./denier ...	5·2–5·8	3·2–4·8	3·3–3·7
Dry elongation, %	14–18	17–24	20–24
Wet elongation, %	15–19	19–28	22–26
Young's modulus, kg./mm.^{2} ...	1,000–1,100	450–800	450–500
Tensile recovery at 2% elongation, %	80–82	74–79	85–88
Specific gravity ...	1·25–1·30	1·25–1·30	1·25–1·30
Regain at 20°c. and 65% R.H., % ...	4·5–5·0	4·5–5·0	3·0–3·5
Softening point in air, °c. ...	220–225	220–225	220–225
Softening point in water, °c. ...	110–125	110–125	110–125
Water absorbency at 95% R.H., %	12–15	12–15	7–10

2. EFFECTS OF ORIENTATION, CRYSTALLINITY, AND ACETALISATION ON DYEABILITY

The aspects of fibre structure which exert a significant influence upon dyeability in general are — (i) molecular orientation in the fibre, (ii) the proportion of amorphous material, and (iii) the chemical constitution of the amorphous region. With regard to (iii), the chemical groups responsible for the attachment of dyes to vinylon are the hydroxyl group and the acetal group. The former

TABLE I

Manufacture of Vinylon

Process	Spinning	Stretching	Heat-treatment	Acetalisation
Main object	Fibre-formation	Increase of tensile strength (orientation)	Resistance to boiling water (First stage— crystallisation)	Resistance to boiling water (Second stage— acetalisation of amorphous portion)
Details	p: 1000–3000 Spinning soln.: 10–20% aq. polyvinyl alcohol Coagulating bath: conc. aq. Na_2SO_4 or aq. $(NH_4)_2SO_4$	(i) Guide stretching (ii) Roller drawing (iii) Wet-heat drawing (in aq. salt bath at 60–100°c.) (iv) Dry-heat drawing (in air or N_2 at 120–230°c.) Combination of (i)–(iv) Draw ratio: 2–15 : 1	(i) Dry heat-treatment (in air or N_2 at 210–240°c.) (ii) Vapour heat-treatment (in H_2O vapour at 120–220°c. and 1–10 atm.) (iii) Wet heat-treatment (in conc. aq. salt bath at 100–160°c.) Under tension, keeping constant length or permitting limited drawing or shrinkage (i–iii), or without tension (crimped fibre) (i and ii)	(i) Formalisation (in aq. soln. of $HCHO + H_2SO_4$ (or $HCl) + Na_2SO_4$ (or $(NH_4)_2SO_4$, or $NaCl$) (ii) Benzalisation (dope-dyeing) (in aq. medium containing $C_6H_5.CHO + H_2SO_4 +$ surface-active agent) Degree of acetalisation: 10–50 mole %
Wet-heat resistance	Marked swelling in water at 20°c. Dissolves in water at 60–85°c.	Shrunk 30–80% in water at 20–50°c., with exception of (iv) at higher temp.	Wet-softening temp. (at which fibre shrinks by 10%): above 80°c.	Wet-softening temp. 100–125°c. Dry-softening temp. 180–225°c.
Molecular arrangement (× = formal group)				

is hydrophilic, conferring dyeing properties resembling those of a cellulosic fibre; but the latter is less hydrophilic, giving vinylon dyeing properties like those of a typical synthetic fibre. Consequently, the dyeing characteristics of vinylon lie in general between those of a cellulosic fibre and those of a typical synthetic fibre. The proportion of amorphous material in vinylon (ii) is markedly affected by stretching, particularly by heat-treatment. Adsorption of dye on the hydroxyl groups in the fibre is greatly influenced, not only by the proportion of amorphous material, but also by the degree of acetalisation in the amorphous region. In regard to (i), stretching exerts a great influence chiefly on the entry and diffusion of dyes into the fibre.

In the following are described the effects of the various manufacturing processes on dyeing properties.

(a) Effects of Formalisation

In the manufacture of vinylon, formalisation is carried out on the heat-treated fibre. The reaction advances from the most accessible region of the fibre to the less accessible regions, and considerable parts of the crystalline region usually remain without being formalised. Since it is the amorphous region that matters in dyeing, it would be insufficient to consider only the degree of formalisation of the fibre as a whole, but this must be considered together with the degree of crystallisation due to heat-treatment. Furthermore, the dyeing properties are affected by the conditions of formalisation [4].

In order to investigate the change in dyeability resulting from replacement of the hydroxyl groups of polyvinyl alcohol by formal groups, we examined the powder obtained by formalising polyvinyl alcohol in aqueous solution, in which the formal groups were considered to be fairly uniformly distributed. The average degree of polymerisation (D.P.) of the polyvinyl alcohol used was 1600. The formalised substances were obtained by stirring an aqueous solution containing 3·2% polyvinyl alcohol, 5% formaldehyde, and 15–35% sulphuric acid at 50°c. for various lengths of time. Dyeability was measured by the following method—

The sample was dyed with 2% (0·4 g./litre) Nippon Fast Violet BB conc. (C.I. Direct Violet 51) with addition of 12·5% (2·5 g./litre) sodium sulphate, in a liquor ratio of 50:1, at 70°c. for 1 hr.; after cooling for about 15 min. to about 20°c., the sample was taken out of the dyebath. It was then rinsed more than a dozen times with water at 20°c., until the washings were no longer coloured. The washings were added to the remainder of the dye liquor, which was then diluted with water to a definite volume more than 1000 times that of the sample. The dye-absorption (g. dye/100 g. fibre) was determined from the extinction of the diluted dye liquor measured by means of a Pulfrich photometer. The peak wavelength of the filter used was 550 mμ. The results are shown in Fig. 1.

With samples having a degree of formalisation below about 75 mole %, the dye was almost completely exhausted from the bath. However,
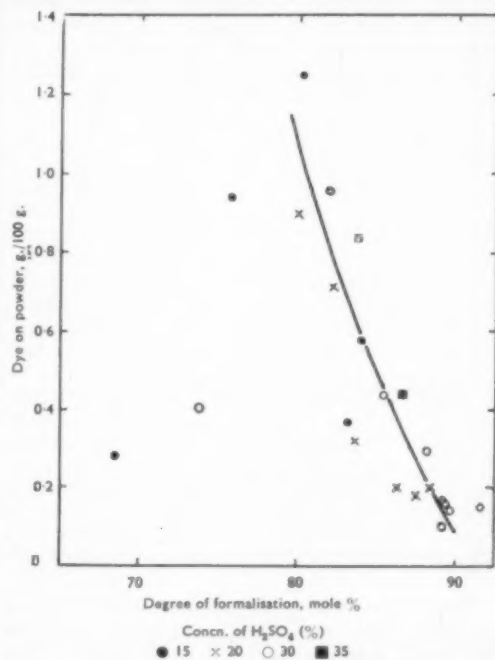

FIG. 1— Relation between Dye-absorption and Degree of Formalisation for Formalised Polyvinyl Alcohol Powders (5% formaldehyde plus sulphuric acid at 50°c.)

these samples were liable to swell, and according to the extent of swelling, part of the absorbed dye was desorbed in the course of rinsing, so that the dyeability of these samples was lower. With more highly formalised products the extent of swelling was lower, so that the desorption of dye during the rinsing was smaller. The dye-absorption begins to fall rapidly at a degree of formalisation of about 80 mole %, and the polymer tends to become almost undyeable at about 90 mole %. The samples obtained by using higher concentrations of sulphuric acid have a slightly higher dye-absorption at a given degree of formalisation, but the relation between dye-absorption and degree of formalisation can be expressed roughly by a single curve.

An unheated wet-spun polyvinyl alcohol fibre was soaked in water at room temperature for 17 hr. without tension. After being squeezed lightly, the sample was formalised in fibrous form at 50°c. for various lengths of time in an aqueous solution containing 5% formaldehyde, 15 or 22·5% sulphuric acid, and 25% sodium sulphate, in a liquor ratio of 30:1 (one-step formalisation). A second sample, which had not been soaked in water, was treated at 50°c. for 5 min. in an aqueous solution of 5% formaldehyde, 10% sulphuric acid, and 25% sodium sulphate, in a liquor ratio of 30:1; the fibre thus formalised to 6·9 mole % was further formalised for various lengths of time under the same conditions as the above one-step formalisation, with 22·5% sulphuric acid (two-step formalisation). The curves of dye-absorption against degree of formalisation are shown in Fig. 2.
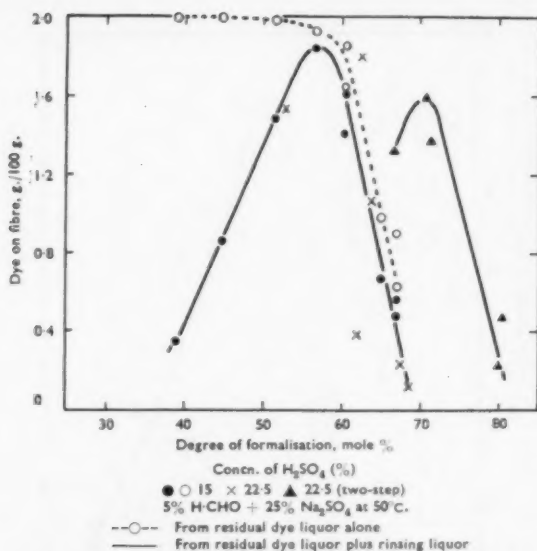
Concn. of H_2SO_4 (%)

● ○ 15   × 22·5   ▲ 22·5 (two-step)

5% H·CHO + 25% Na_2SO_4 at 50°C.

--○--   From residual dye liquor alone

——   From residual dye liquor plus rinsing liquor

FIG. 2 — Relation between Dye-absorption and Degree of Formalisation for Formalised Products of Unheated Polyvinyl Alcohol Fibre

For the one-step formalisation products obtained by using 15% and 22·5% sulphuric acid, the relation is represented by a single curve. The dye-absorption falls rapidly at a degree of formalisation of about 60 mole %, and an almost undyeable state is reached at about 70 mole %. On the other hand, in the two-step formalisation products, the curve is shifted to higher degrees of formalisation by about 10 mole %. The lower dye-absorption in the region of lower degrees of formalisation is due to the same cause as in the case of the formalised powder. With the one-step formalisation products, the dye-absorption determined from residual dye in the bath without rinsing is shown by the dotted curve in Fig. 2. It is apparent that in the range of higher degrees of formalisation, where the curve is falling, the effect of rinsing on the dye-absorption is fairly small.

These formalised powders and fibres were subjected to swelling in aqueous phenol solution, and after thorough rinsing the dye-absorption was measured. Also, samples were reformalised before and after swelling with phenol, and the degree of formalisation and the dye-absorption were determined. The results are shown in Table III. For comparison, results obtained with a heat-treated fibre are included.

The formalised powder derived from the aqueous solution of polyvinyl alcohol shows no significant difference in degree of formalisation between products reformalised with and without the swelling treatment, but with the fibre formalised to a fairly high degree, a higher degree of formalisation is imparted when reformalisation is carried out after swelling, compared with the unswollen fibre, irrespective of whether the fibre has been heat-treated or not. With regard to dye-absorption, in the case of formalised powder swelling causes no significant increase, but in the case of formalised fibre the dye-absorption is markedly increased by swelling, though it falls after reformalisation. With both formalised powders and fibres, apparent swelling by phenol could be clearly recognised.

From the above results, it is suggested that in formalised fibre, even without heat-treatment, the distribution of formal groups is quite irregular, that a fairly large proportion of the unsubstituted hydroxyl groups are in an inaccessible state, and that some of them become accessible on treatment with phenol. In the formalised powder, on the other hand, since formalisation proceeds in the homogeneous solution up to at least about 40 mole %, the distribution of formal groups is probably fairly homogeneous, the unsubstituted hydroxyl groups are not particularly inaccessible, and no appreciable increase in the accessibility of the hydroxyl groups results from the swelling. Accordingly, the curve in Fig. 1 may well be regarded as showing the dyeing behaviour towards direct dyes of polyvinyl formal containing only formal groups and accessible hydroxyl groups.

TABLE III

Treatment of Formalised Products with Phenol

Type of Sample	Formalising Bath			Degree of Formalisation (mole %)			Dye-absorption (g./100 g.)			
	HCHO (%)	H_2SO_4 (%)	Na_2SO_4 (%)	Original	Reformalised without Phenol Treatment	after† Treatment	Original	Treated with Phenol*	Reformalised without Phenol Treatment	after† Treatment
Powder	10	20	0	75·0	89·9	83·1	—	—	1·8	2·5
	5	20	0	82·2	84·6‡	84·2‡	7·1	6·1	3·1‡	2·7‡
	5	20	0	86·4	86·3‡	86·3‡	2·0	1·6	1·3‡	2·5‡
	5	30	0 ⎫§	89·3	92·5	93·1	1·7	1·6	2·4	1·6
	5	40	5 ⎭							
Unheated fibre	5	15	25	54·4	63·9	68·6	17·0	16·5	3·6	5·1
	5	15	25	64·6	68·1	79·7	3·9	15·2	4·6	4·3
	5	22·5	25	73·6	77·6	83·5	2·8	17·2	2·1	1·6
	5	22·5	25	74·7	76·7‡	83·6‡	—	15·6	2·4‡	1·5‡
	5	22·5	25	79·9	—	—	2·3	12·6	—	—
Heat-treated fibre	5	20	0	49·5	51·4	63·2	0·2	14·5	1·3	1·4

*   The original formalised samples are treated at 20°C. in 5% aq. phenol soln. (liquor ratio 100 : 1) for 30 min.

†   The reformalised samples are treated at 50°C. in a similar bath for 25 hr.

‡   Duration of phenol treatment 45 hr.

§   Upper row refers to original samples; lower row to reformalised samples.

(b) *Effects of Heat-treatment and Stretching*

The effects will be described of crystallinity and orientation on dyeability, both alone and in combination with formalisation.

To begin with, the effects of heat-treatment on dyeability will be described. A wet-spun polyvinyl

alcohol tow (4 denier × 600 filaments × 10) was heat-treated in the air at various temperatures for various lengths of time, the original length being maintained, and was dyed in the same manner as previously described. Fig. 3 and 4 show the results.

In Fig. 3, for a heating time of 5 min., the dye-absorption becomes greater as the temperature of heat-treatment is raised in the lower range of temperatures, passes through a maximum at about 200°c., then falls to a minimum at about 220°c., and increases again with further rise in temperature. As is shown by the dotted line in Fig. 3, the fibre heat-treated at 180°c. absorbs a greater amount of dye than does that heat-treated at 200–230°c., but much of this is desorbed owing to the swelling of the former fibre during rinsing. The decrease in dye-absorption in the temperature range from 200° to 220°c. seems to be due to increase in crystallinity. The increase in dye-absorption from 220° to 230°c. may be attributable to degradation of the fibre. Table IV shows the tensile strength and elongation of these heat-treated fibres. It may be noticed that the strength falls markedly with the fibre heat-treated at 230°c. for 5 min. The results of Fig. 4 can be interpreted in a similar way.

FIG. 3— Relation between Dye-absorption and Temperature of Heat-treatment (time of heating 5 min.)

○ From residual dye liquor alone
● From residual dye liquor plus rinsing liquor

TABLE IV
Tenacity and Elongation of Heat-treated Fibre
(Samples heat-treated for 5 min.)

Heating Tempera-ture (°c.)	Dry Tenacity (g./denier)	Dry Elonga-tion (%)	Wet Tenacity (g./denier)	Wet Elonga-tion (%)
Unheated	2·33	18·3	—	—
150	2·74	22·3	—	—
180	2·96	18·5	1·34	23·3
200	2·44	21·4	—	—
210	2·64	20·6	—	—
220	2·80	22·4	2·09	26·6
230	1·71	24·5	1·21	31·0

These heat-treated fibres were subjected to formalisation at 50°c. for various lengths of time in aqueous solutions containing 5% formaldehyde, 15% sulphuric acid, and 25% sodium sulphate, in a liquor ratio of 30 : 1, and the dye-absorption was measured with these formalised fibres likewise. The dyeing behaviour (Fig. 5 and 6) may be explained on the above lines.

Next, the effect of the formalising conditions on the dyeability of the heat-treated fibre was studied[5]. The fibre, heat-treated at 220°c. for 5 min., was formalised in aqueous solutions containing formaldehyde, sulphuric acid, and sodium sulphate, at a liquor ratio of 30 : 1, without tension, and the dye-absorption was measured. The results are shown in Fig. 7–9.

Fig. 7 illustrates the effect of concentration of sulphuric acid. With the formalised products derived from aqueous solutions of polyvinyl alcohol and from the fibre without heat-treatment, the relations between dye-absorption and degree of formalisation were hardly affected by the concentration of sulphuric acid, and could be expressed almost by a single curve (Fig. 1 and 2). With the heat-treated fibre, however, the relations
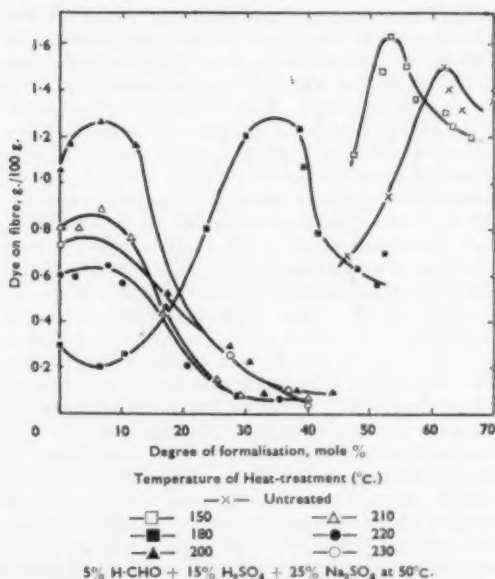

Temp. of Heating (°C.)
■—■ 180
▲—▲ 200
△—△ 210
●—● 220
○—○ 230

FIG. 4— Relation between Dye-absorption and Duration of Heat-treatment

FIG. 5— Effect of Temperature of Heat-treatment (time of heating 5 min.) on Relation between Degree of Formalisation and Dye-absorption

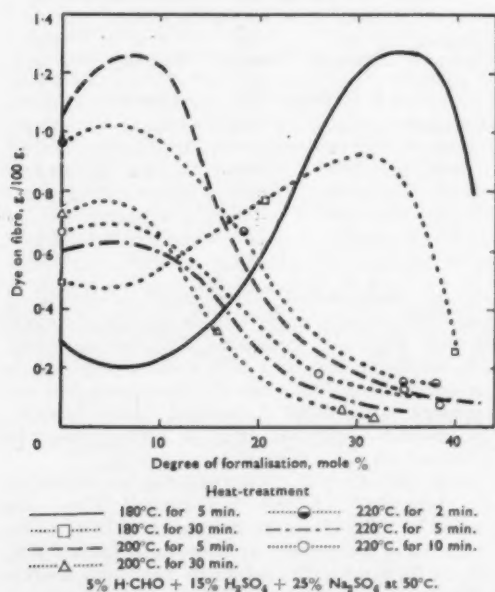FIG. 6— Effect of Duration of Heat-treatment on Relation between Degree of Formalisation and Dye-absorption

FIG. 7— Effect of Concentration of Sulphuric Acid on Relation between Degree of Formalisation and Dye-absorption
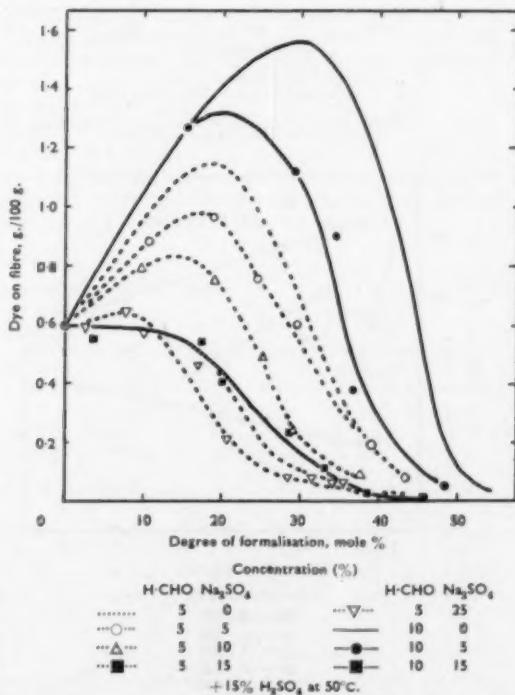
FIG. 8— Effect of Concentration of Sodium Sulphate in Formalising Bath on Relation between Dye-absorption and Degree of Formalisation

are greatly affected, the dye-absorption being increased as the concentration becomes higher. The dye-absorption shows a maximum at a certain degree of formalisation, which shifts to higher values as the conditions of reaction become more favourable to intensified swelling (Fig. 8 and 9 show this more distinctly). In the case of heat-treated fibres there is no appreciable difference between dye-absorptions determined with and
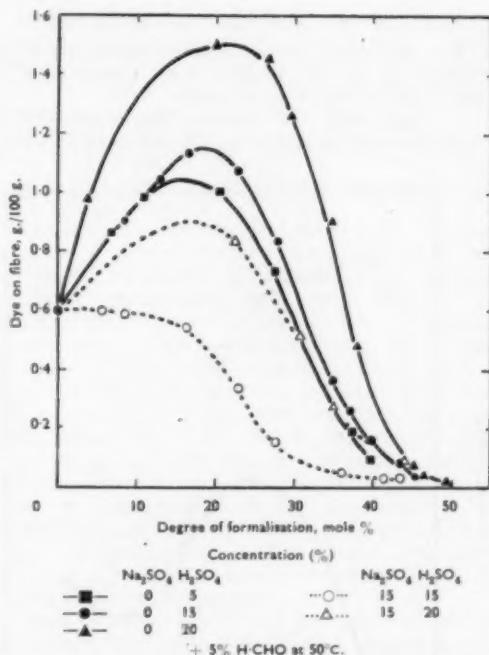
FIG. 13— Cross-section of Ordinary Formalised Vinylon (× 500)
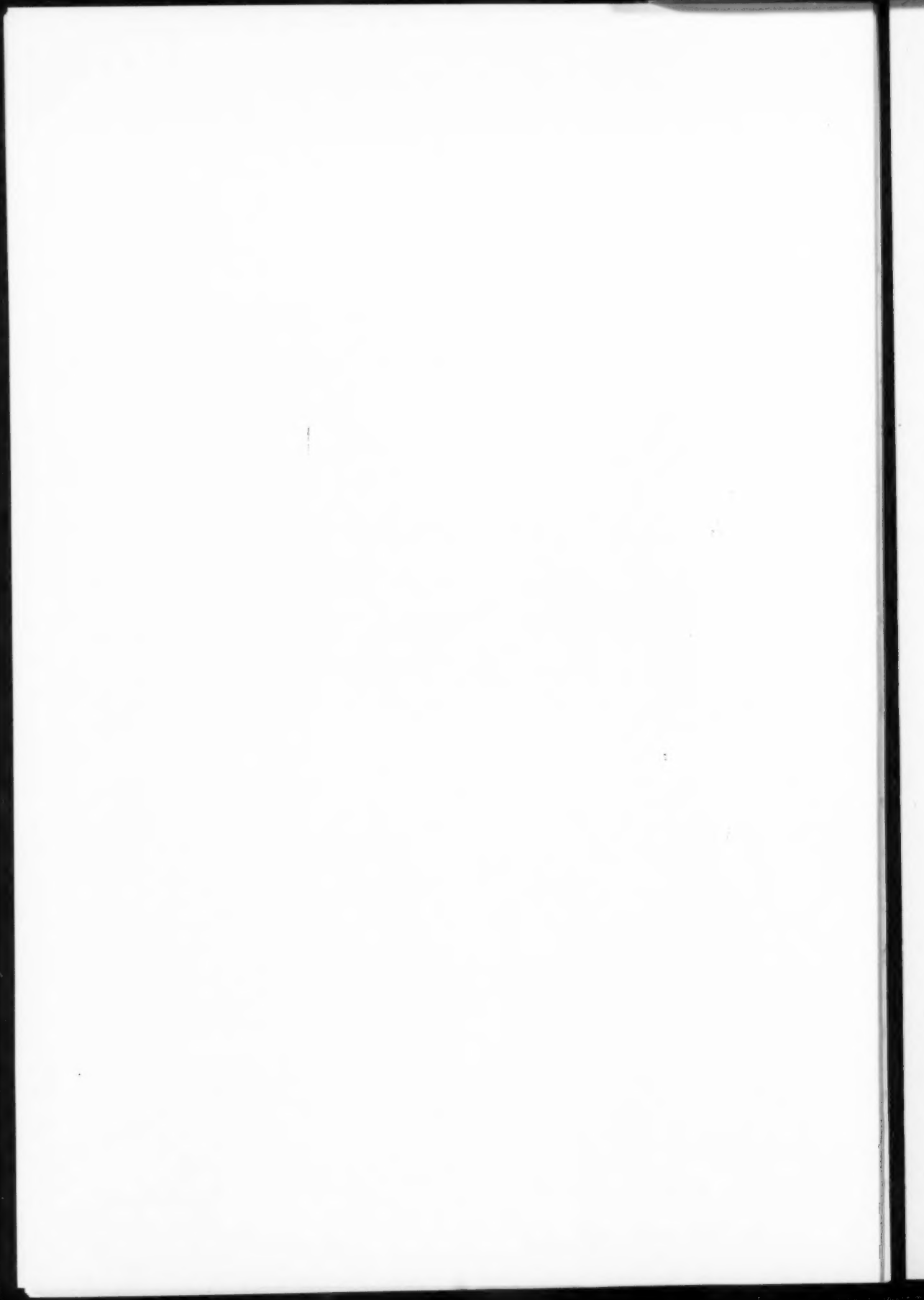
without rinsing after dyeing, and the increase in the dye-absorption is observed at an earlier stage of formalisation. This suggests that, in the range of lower substitutions, the effect of the enlargement of the dye-accessible region due to the swelling during formalisation masks that of the blocking of hydroxyl groups due to the formalisation itself, whereas the effect of the latter prevails as the substitution proceeds further.

In the series of experiments with 15% sodium sulphate, the increase of dye-absorption in the earlier stage of formalisation and the dye-absorption itself are smaller than in the absence of sodium sulphate, so that it would appear that swelling during formalisation is less in the presence of sodium sulphate. Fig. 8 confirms the considerable improvement in dyeability achieved by lowering the concentration of sodium sulphate. Also, 10% formaldehyde gives better dyeability than 5%, especially in the absence of sodium sulphate. Under the same dyeing conditions, the dye-absorptions for cotton and viscose rayon staple fibre are 0·9 and 1·15 g./100 g. respectively. Vinylon equivalent to cotton in dyeability can be obtained from the series with 5% formaldehyde and no sodium sulphate, and fibre equivalent to viscose rayon staple fibre from 10% formaldehyde and no sodium sulphate, both having adequate resistance to boiling water.

Fig. 9 illustrates the effects of concentration of formaldehyde and formalising temperature: the greater the concentration of formaldehyde and the higher the temperature, the better the dyeability.

With regard to the effects of the conditions of formalisation on resistance to dry and to wet heat, tenacity, and elongation, the more the conditions of reaction are likely to cause swelling, the lower the wet- and dry-heat resistances and the tenacity, while elongation tends to be greater. However, the effects on these fibre properties are smaller than the effect on the dyeability. An example is given in Table V.

In order to examine the effects exerted when stretching is applied, a wet-spun polyvinyl alcohol tow (6 denier × 100 filaments × 1) was drawn to 0, 200, and 370% in hot air at 230°C. for 30 sec., and the three samples were then heat-treated at 235°C. for 30 sec., the drawn length being maintained. They were subsequently formalised in a 50:1 aqueous solution containing 5% formaldehyde and 15% sulphuric acid, but no sodium sulphate, at 50°C. for various lengths of time, and the degree of formalisation and the dye-absorption were measured in the same manner as before. From Fig. 10 it is clear that, as the draw ratio increases, the dyeability falls.

The results discussed above show that both heat-treatment and stretching can alter dyeability, and it is of particular interest that the dyeability of products obtained by formalising in fibrous form is quite different from that of formalised powders derived from aqueous solutions of polyvinyl alcohol, being affected not only by the degree of formalisation but also by the conditions of formalisation. In conclusion, the dyeability of vinylon can be said to be determined by the

TABLE V

Effect of Concentration of Sodium Sulphate in Formalising Bath on Properties of Fibre

(+5% H·CHO + 15% H_2SO_4)

Time of Formalisation (hr. min.)		Degree of Formalisation (mole %)	Shrinkage in Boiling Water (%)	Softening Point in Air (°C.)	Dry Tenacity (g./denier)	Dry Elongation (%)	Dye-absorption (g./100 g.)
			NO SODIUM SULPHATE				
	10	13·0	56	216	2·49	28·6	1·04
	15	16·7	43	—	—	—	1·13
	30	22·8	5·0	—	2·66	21·4	1·07
1		27·8	7·5	214	—	—	0·83
3		35·1	5·5	—	—	—	0·36
5		37·0	4·0	215	—	—	0·26
10		40·1	6·8	—	2·63	19·7	0·16
25		43·7	7·7	—	—	—	0·08
			15% Na_2SO_4				
	10	8·4	60	—	3·39	22·9	0·59
	15	16·3	60	—	—	—	0·54
	30	22·9	8·5	—	2·84	27·2	0·33
1		27·5	1·3	—	—	—	0·15
5		36·0	1·5	—	—	—	0·05
25		41·5	3·8	—	3·10	23·2	0·03
			25% Na_2SO_4				
	10	7·8	63	—	2·72	20·4	0·64
	15	9·9	55	216	—	—	0·57
	30	17·0	52	—	—	—	0·46
1		20·4	54	211	3·12	17·3	0·21
3		28·6	4·7	—	—	—	0·08
5		31·4	5·0	225	3·20	15·0	0·08
10		33·9	4·2	—	—	—	0·06
25		35·4	2·2	—	—	—	0·06

A7

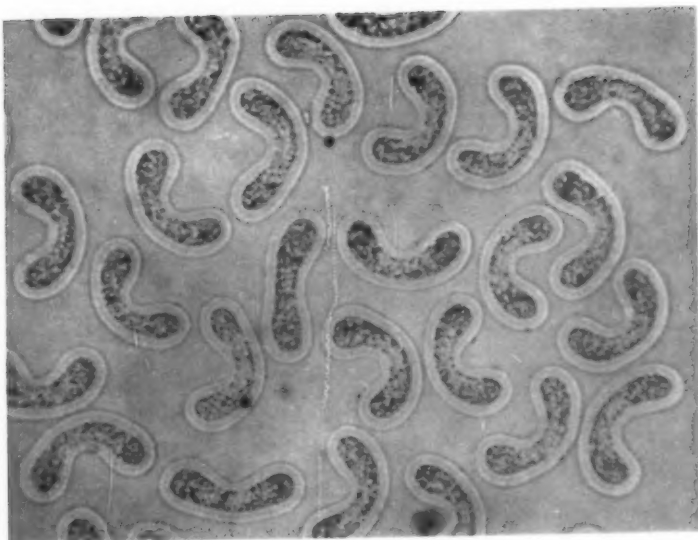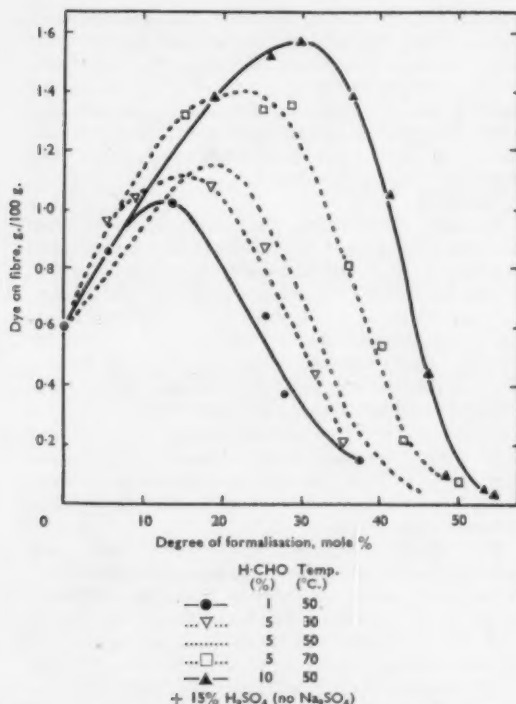|	H·CHO (%)	Temp. (°C.)
—●—	1	50
...▽...	5	30
....	5	50
...□...	5	70
—▲—	10	50
+ 15% H_2SO_4 (no Na_2SO_4)		

FIG. 9— Effect of Concentration of Formaldehyde and Formalising Temperature on Relation between Dye-absorption and Degree of Formalisation
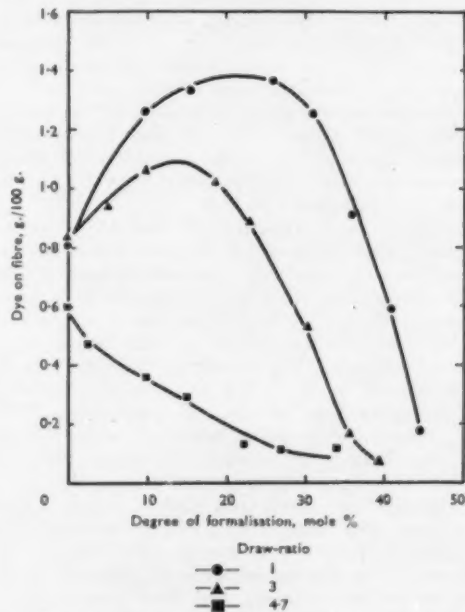

Draw-ratio
—●— 1
—▲— 3
—■— 4·7

FIG. 10— Effect of Heat-drawing on Relation between Dye-absorption and Degree of Formalisation

previous history of the polyvinyl alcohol fibre, i.e. by the orientation and the crystallinity, as well as by the distribution in the amorphous region of the acetal groups resulting from formalisation.

(c) Effects of Acetalisation with Other Aldehydes

It has already been shown that the elastic recovery can be improved by acetalising polyvinyl alcohol fibre with aldehydes higher than formaldehyde [6,7] (cf. Fig. 11). The relations between dye-absorption and degree of acetalisation for various aldehydes are given in Fig. 12. Acetaldehyde yields a fibre with better dye-absorption than the formalised fibre. But with propionaldehyde or butyraldehyde the degree of acetalisation at which the dye-absorption reaches a maximum is shifted to markedly lower values. Furthermore, the degree of acetalisation at which the fibre is left almost unstained is also much lower. With benzaldehyde these trends are even more evident. Consequently, benzalised vinylon is now coloured by dope-dyeing.

It is also well known that by acetalising polyvinyl alcohol fibre with a dialdehyde, e.g. glyoxal [8], acetalyl
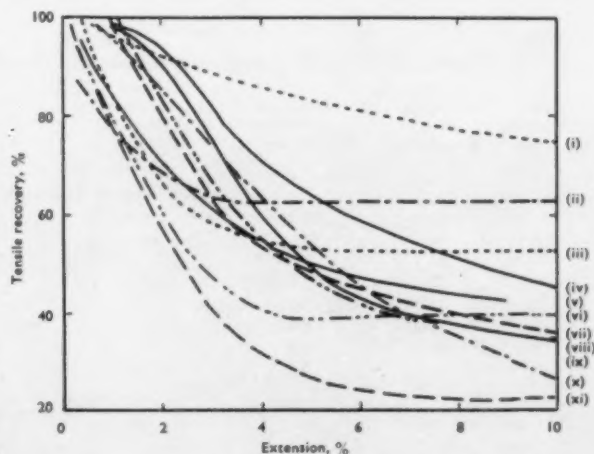
		Fibre	Aldehyde	Degree of Acetalisation (mole %)
(i)	....	Nylon	—	—
(ii)	—·—·—·	Vinylon	—	—
(iii)	....	Vinylon	Formaldehyde	35·3
(iv)	————	Wool	—	—
(v)	————	Silk	—	—
(vi)	–·–·–·–	Cotton	—	—
(vii)	————	Vinylon	n-Butyraldehyde	35·2
(viii)	————	Vinylon	Benzaldehyde	30·7
(ix)	–·–·–·–	Vinylon	isoValeraldehyde	30·2
(x)	—··—··—	Cellulose acetate	—	—
(xi)	— — —	Viscose rayon	—	—

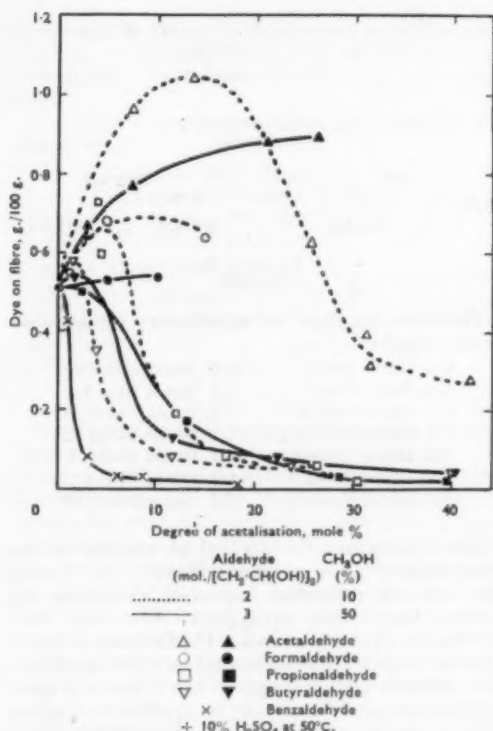FIG. 11— Effect of Acetalisation with Higher Aldehydes on Tensile Recovery

FIG. 12— Effect of Acetalisation with Higher Aldehydes on Relation
between Dye-absorption and Degree of Acetalisation

sulphides[9], and phthaldehydes[10], better wet-heat resistance can be obtained than with formalised vinylon. Thus, for formalised vinylon the wet-softening temperature is 110–125°c., whereas for vinylon acetalised with a dialdehyde it is generally raised to 100°c. at a degree of acetalisation of about 6 mole % (computed from the weight increase due to the reaction by assuming that all bound dialdehydes are cross-linked between molecules of polyvinyl alcohol), to 120°c. at about 13 mole %, and to 140°c. at about 20 mole %. However, their dyeability is very low, the dye-absorption being less than 0·1 g./100 g. at 10 mole %.

3. ANIMALISATION OF VINYLON

Since vinylon contains no basic nitrogen, it cannot be dyed with acid wool dyes, and many attempts have been made at the animalisation of vinylon. The methods employed can be classified as (*a*) polymer blending and (*b*) chemical after-treatment. In (*b*) basic nitrogen is introduced by means of various chemical reactions. Thus Sakurada[11] discovered a method in which heat-treated fibre was acetalised with chloroacet-aldehyde, and then treated with ammonia or ethylenediamine. Ohsugi *et al.*[12] acetalised heat-treated fibre with an aminoaldehyde, e.g. aminopropionaldehyde or β-*cyclo*hexylaminobutyr-aldehyde, and then formalised or benzalised it. With regard to method (*a*), Ohsugi *et al.*[13] developed a method in which an aqueous solution

of a mixture of polyvinyl aminoacetal and poly-vinyl alcohol was used as the spinning solution.

4. MODIFICATION OF MICROSCOPICAL STRUCTURE

The cross-section of vinylon is illustrated in Fig. 13. With most dyes the core is more heavily dyed than the skin. As a result, the tinctorial value (depth of colour corresponding to a given dye-absorption) is not good enough, and attempts are being made to obtain a fibre having an optically homogeneous cross-section. The fibre produced by dry-spinning achieves this object. Also the wet-spun fibre derived from a polymer blend shows some improvement in tinctorial value in most cases.

III— The Scouring and Bleaching of Vinylon

1. SCOURING

Scouring may be carried out in the same manner as with any of the usual man-made fibres. The wet-softening temperature of vinylon is usually 110–125°c., but in order to safeguard the fibre against shrinkage, harsh handle, and yellowing, the wet-treatment of vinylon is, as a rule, preferably carried out below 95°c. without tension. Generally, it can be satisfactorily scoured in an aqueous solution containing 1–3 g. of alkyl sulphate per litre at 80°c. for 30 min.

2. BLEACHING

The whiteness of vinylon as tow is generally 92–94% of that of magnesium oxide, and as crimped fibre 85–88%. Where medium or heavy dyeing is to be carried out, preliminary bleaching is not needed. However, bleaching is desirable in the case of pale dyeings.

The bleaching agent is sodium hypochlorite, or preferably sodium chlorite and a fluorescent brightening agent. For vinylon–wool blends hydrogen peroxide also may be used. When sodium hypochlorite is used, the goods are soaked in an aqueous solution, containing 3–5 g. of available chlorine per litre, at ordinary temperature for 10–30 min., squeezed to three times the dry weight of the goods, treated in 3–5 g. of sulphuric acid per litre at 30–50°c. for 10–30 min., and then rinsed thoroughly. If the rinsing is inadequate, so that free chlorine may remain in the fibres, then yellowing may occur during drying. Therefore, it is desirable to treat the goods with sodium thiosulphate. As sodium chlorite is known to be a milder oxidising agent than sodium hypochlorite, the former is more suitable for vinylon.

Bleaching with sodium chlorite is carried out either by the one-bath method or by the two-bath method. For example, in a bleaching bath containing 1·5–2·0 g. available chlorine and 3–6 g. acetic acid or 0·5–1 g. sulphuric acid per litre, the goods are treated in a 20–50:1 liquor at 60–70°c. for 30 min., and then rinsed thoroughly. In the latter method, the goods are soaked in a bleaching bath containing 5 g. available chlorine per litre at ordinary temperature for 10–30 min., squeezed to about three times their dry weight, treated in 0·5 g. sulphuric acid per litre at 70°c. for 30 min., and then rinsed thoroughly.

When a very good white is required, the use of fluorescent brightening agents is preferred. Uvitex WS and NL, Leucophor B, BS, WS, and S Special, Tinopal AN, Tintofen W highly conc. (G), and Ultraphor WT (C.I. Fluorescent Brightening Agents —, 62, 32, 49, 52, —, 55, —, and 48) are cited as suitable for vinylon.

IV— The Dyeing of Vinylon

As previously mentioned, vinylon has dyeing properties intermediate between those of cellulosic fibres and synthetic fibres, so that, on the one hand, direct, sulphur, vat, and azoic dyes may be used, and on the other, disperse and metal-complex dyes may be applied to vinylon. As these different groups have characteristic colouring effects, the one most suitable for the specific purpose should be selected.

The synthesis of dyes for vinylon has been studied mainly in Japan, and future developments are expected in this field of research. The discussion which follows is restricted to the behaviour of the formalised vinylon now on sale in dip dyeing with available dyes on which the authors have experimented.

1. DIRECT DYES

Vinylon is comparable with cotton or viscose rayon in its absorption of some direct dyes, but with others it shows fairly poor absorption; thus it differs from cellulosic fibres in that its dyeability with direct dyes varies widely from dye to dye. For vinylon, generally speaking, dyes containing many sulpho groups, particularly more than three, have poor substantivity, while those which contain a larger number of amino groups than of sulpho groups tend to show better substantivity. Thus dyes (i)–(iii) have better substantivity for vinylon than have (iv)–(vi) respectively.
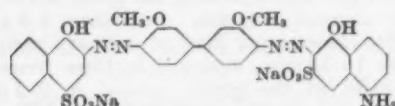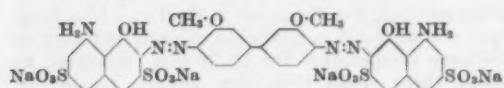

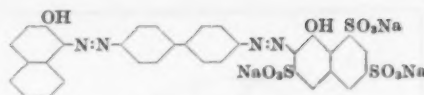(i)   C.I. Direct Blue 12
(C.I. 24170)
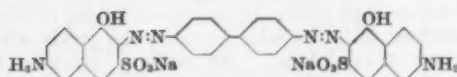
(ii)   C.I. Direct Violet 12
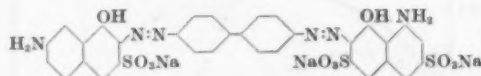(C.I. 22550)
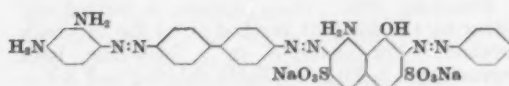
(iii)   C.I. Direct Black 38
(C.I. 30235)

(iv)   C.I. Direct Blue 15
(C.I. 24400)

(v)   C.I. Direct Violet 22
(C.I. 22480)

(vi)   C.I. Direct Blue 2
(C.I. 22590)

The following dyes are satisfactory for application to vinylon—

C.I. Direct Red 1	C.I. Direct Green 8
C.I. Direct Red 2	C.I. Direct Blue 12
C.I. Direct Red 28	C.I. Direct Violet 11
C.I. Direct Yellow 1	C.I. Direct Violet 12
C.I. Direct Orange 7	C.I. Direct Brown 1
C.I. Direct Green 1	C.I. Direct Brown 2
C.I. Direct Green 6	C.I. Direct Black 38

Direct dyes may be applied to vinylon in the same manner as to cellulosic fibres. The dyeing effect can be somewhat improved by raising the dyeing temperature to approx. 90°c. and then leaving the dyebath to cool. The fastness of direct dyes on vinylon is similar to that on cellulosic fibres. The methods used to improve the fastness of dyeings on cellulosic fibres may be applied to vinylon with a closely similar effect. Coprantine (Ciba) dyes, which are claimed to be a range of direct dyes with good fastness, show fairly good dye-absorption, but the promotion of fastness by the use of Coprantex B (Ciba) is not so effective as with cellulosic fibres. Cuprofix (S) and Sirius (FBy) dyes do not show sufficiently high dye-absorption.

2. SULPHUR DYES AND SULPHUR VAT DYES

Like direct dyes, sulphur dyes show a wider variation in substantivity on vinylon than on cellulosic fibres. Generally speaking, blue dyes show good absorption, but sulphur blacks have poor substantivity. With other sulphur dyes, generally, the substantivity on vinylon is inferior to that on cellulosic fibres. Blue or black dyeings produced with sulphur dyes on vinylon tend to be more reddish than the corresponding dyeings on cellulosic fibres. As a remedy for this, after-treatment with an aqueous solution of stannous chloride or ferrous sulphate may be applied with some success.

The same dyeing method may be employed as for cellulosic fibres, except that the dyeing temperature is preferably somewhat higher, say 80–90°c. In heavier dyeings bronzing is liable to occur, which can be restrained to some extent by addition of a non-ionic surface-active agent to the dye-bath. For black dyeings, as sulphur black dyes may yield only a grey, the use of sulphur vat dyes is desirable. It is not easy to produce full blacks even with dyes of this type, so that dope-dyeing is now the most useful method. As reducing agents for sulphur vat dyes, ammonia and sodium

hydrosulphite, sodium sulphide and sodium hydro-sulphite, or thiourea dioxide are found to be more suitable than sodium sulphide alone in certain cases.

The following sulphur dyes are suitable for dyeing vinylon—

> Sulfogene (DuP) dyes
> C.I. Sulphur Orange 4
> C.I. Sulphur Blue 13
> C.I. Sulphur Black 4

So-Dye-Sul (SDC) dyes, which are water-soluble sulphur dyes, Immedial Special (CFM) dyes, with which a weak alkaline reducing agent can be used, and Thionol (ICI) dyes produce fairly good colouring effects on vinylon.

3. VAT DYES

The dyeability of vinylon with vat dyes is somewhat inferior to that of cotton. Therefore, vat dyes are used for pale–medium dyeings requiring excellent fastness. The dyeing methods may be the same as with cellulosic fibres, but in some cases a higher dyeing temperature is preferable. When satisfactory colour development cannot be attained by air oxidation, use of hydrogen peroxide may prove more effective. Also, the vat acid method seems to be useful.

Some examples of vat dyes which show relatively good dyeing effects are given below—

C.I. 60750	C.I. Vat Green 9
C.I. Vat Red 1	C.I. Vat Blue 4
C.I. Vat Orange 9	C.I. Vat Blue 43
C.I. Vat Yellow 2	C.I. Vat Violet 1
C.I. Vat Green 1	

4. AZOIC DYES

The dyeing methods used for cellulosic fibres yield unsatisfactory results on vinylon, but those adopted for cellulose acetate or synthetic fibres yield good effects. The goods are worked in an alkaline bath containing both diazo and coupling components at 70–80°c., and then developed in a bath containing sodium nitrite and acetic acid, formic acid, or an inorganic acid at 10–20°c. For example, the goods are treated in a 40:1 bath containing, per litre—

2	g. ...	C.I. Azoic Coupling Component 4
0·95	g. ...	C.I. Azoic Diazo Component 48
3	c.c.	Methanol
0·8	g. ...	Sodium hydroxide
20	g. ...	Sodium sulphate

together with a small amount of Turkey Red oil or other surface-active agent, at 75°c. for 60 min., and rinsed lightly. Then they are developed in a 40:1 bath containing 5 g. sodium nitrite and 25 c.c. glacial acetic acid per litre at 15–20°c. for 30–60 min., and soaped. This method is suitable for the production of pale–heavy dyeings of satisfactory brightness in various colours by using different combinations of coupling components and diazotisable bases, but rubbing fastness is rather poor, particularly in such colours as red, bordeaux, and garnet. Besides the ordinary azoic dyes, Acetoquinone Diazo (Fran) dyes and Eastman (TE) dyes can also be applied with similar

dyeing effects. Farbwerke Hoechst offer this type of dye for vinylon in several colours, which are used in practice.

5. DISPERSE DYES

Disperse dyes, e.g. Celliton (BASF) and Dispersol (ICI) dyes, are absorbed fairly well, but the fastness is unsatisfactory, which greatly limits their application. This type of dye, especially when applied to vinylon, not only has poor wash fastness, but also has the disadvantage of staining white goods with which the dyed goods are in contact during storage.

6. METAL-COMPLEX DYES

Dyes of this type, particularly the recently developed 2:1 class, in which each metal atom is associated with two azo groups, can give dyeings of at least medium depths with excellent fastness. Good dyeings can be produced with the Lanasyn (S), Irgalan (Gy), Cibalan (Ciba), Vialon (BASF), Capracyl (DuP), and Isolan (FBy) ranges. This is now one of the most suitable classes of dyes for vinylon.

7. BASIC DYES

Vinylon can be dyed with or without tannin mordant. However, as the light fastness is not good enough, they are rarely applied, except for special uses.

8. ACID AND MORDANT DYES

These two groups of dyes cover a wide range of substantivity for vinylon, from those yielding medium depths to those which can hardly stain vinylon. However, the wash fastness of acid dyes on vinylon is very poor compared with that on wool. Good fastness can be obtained with acid mordant dyes, so some of them may be utilised for pale–medium dyeings, for which the after-chroming method is adopted.

When vinylon is treated with an aqueous solution containing 5–10% sodium dichromate, 1–0·5% sulphuric acid, and 20% sodium sulphate at 80°c. for 60 min., 0·5–2·0% chrome on the weight of fibre remains combined with the vinylon. The combined chrome is fairly stable. The mechanical properties of the fibre may suffer slightly from the treatment, but the dyeing properties for direct and acid mordant dyes are considerably improved.

Selected dyes from the Carbolan (ICI), Coomassie (ICI), Xylene Fast P (S), and Solway (ICI) ranges give dyeings of medium depths, but the wash fastness is still not satisfactory. On animalised vinylon, these dyes give deep dyeings of excellent brightness and fairly good fastness, and seem to offer good prospects for future development on such fibres.

9. SPECIAL DYEING METHODS

In recent years, various special dyeing methods have been devised for synthetic fibres which are difficult to dye. High-temperature dyeing does not offer any particular advantages for vinylon, since its wet-heat resistance is comparatively low, and vinylon fabrics are apt to shrink and acquire a

harsh handle when subjected to wet treatments above 100°c. A swelling method, in which phenol or cresol is used as swelling agent, is frequently found useful. The goods are treated in an aqueous solution containing 3–5% phenol at 30°c. for 30 min. After thorough rinsing, the goods are dyed. By this method, the mechanical properties of the fibre are slightly impaired, but its dyeability is considerably improved. This method is found especially useful for sulphur or vat dyeing.

10. THE DYEING OF BLENDS

In order to obtain solid shades with vinylon–cellulosic fibre blends, direct, sulphur, sulphur vat, or vat dyes are used. Shading is done by dyeing the vinylon with metal-complex or disperse dyes.

Multicoloured effects can be obtained by dyeing the cellulosic fibre with direct blue, sulphur black, etc. dyes, which have practically no substantivity for vinylon, and the vinylon with metal-complex or disperse dyes.

In the case of vinylon–wool blends, it is desirable to dye each fibre separately in loose or top form before blending. Dyeing after blending may be carried out either by the use of metal-complex dyes for both fibres, or by applying acid or acid mordant dyes to the wool, and then disperse dyes to the vinylon.

V— Dope Dyeing

From the above discussion it is apparent that vinylon can be readily dyed in pale–medium depths, but deeper colours, such as black, navy blue, and brown, are generally difficult to achieve with satisfactory fastness. It is therefore found that dope-dyeing is easier and more advantageous for obtaining these deep colours. Thus the Kurashiki Rayon Co. has produced dope-dyed vinylon on a commercial scale.

The main problems to be taken into consideration in the dope-dyeing of fibres in general are size of pigment particles, stability of pigment paste or emulsion, feasibility of continuous supplies of pigment of constant quality, stability of the spinning solution (so that change in viscosity, gelation, settling of pigments, separation of pigment blends, etc. do not take place), good filtration properties, satisfactory colour fastness (to light, rubbing, washing, etc.), and reasonable price. With vinylon the following additional problems are encountered— (1) Compared with a viscose spinning solution, a polyvinyl alcohol spinning solution is kept at a remarkably high temperature (in wet-spinning up to 100°c., and in dry-spinning up to 130°c.), so its stability and spinnability at such high temperatures must be considered. (2) The spun fibre is subsequently subjected to heat-treatment. Therefore, the pigments and the auxiliary agents used should maintain their stability during dry-heating at 240°c. for 10 min. (discoloration, sublimation, decomposition, etc. should not occur), and further these substances must be inert towards polyvinyl alcohol (they should not cause yellowing or decomposition of polyvinyl alcohol). (3) The heat-treated fibres are then subjected to formalisation

or benzalisation, so the pigments are required to be stable and resistant to these acetalising processes, i.e. to an aqueous solution containing 20% sulphuric acid and 5% formaldehyde, or 10% sulphuric acid, 2% benzaldehyde, and 1% surface-active agent, at 80°c. for 60 min. (4) Finally, a given depth of colour should be attained by using as small a quantity of pigment as possible.

This company is now manufacturing black and dark blue fibres for students' and other uniforms. The pigments used fulfil the above requirements in both the manufacturing processes and the quality of the products. Besides the above, vinylon coloured maroon, green, or light blue is produced for moquette. The company contemplates the production of other colours, and expects that pigments to meet the above-mentioned requirements will make their appearance.

*   *   *

KURASHIKI RAYON CO. LTD.
  2 UMEDA
    KITAKU
      OSAKA
        JAPAN

References

[1] Herrmann, W. O., and Haehnel, W., Ber. deutsch. chem. Ges., 60, 1658 (1927).

[2] Herrmann, W. O. (Consortium Elektrochemische Industrie GmbH.), FP 732,895 (1932); BP 386,161.

[3] Lee, S., Kawakami, H., and Hitomi, K., Ann. Rep. Japan Inst. Chem. Fibres, 5, 115 (1940);
Japan Inst. Chem. Fibre Inc., Japanese Patent 157,076;
Yazawa, M., and Ogino, C., J. Soc. Chem. Ind. Japan, 47, 549, 551 (1944);
Kanegafuchi Boseki Co., Japanese Patent 153,812.

[4] Tanabe, K., and Morimoto, O., J. Soc. Textile Cellulose Ind. Japan, 11, 86 (1955).

[5] Idem, ibid., 11, 91 (1955);
Ohsugi, T., Tanabe, K., and Morimoto, O. (Kurashiki Rayon Co.), BP 737,130.

[6] Tanabe, K., and Ohno, K., J. Soc. Textile Cellulose Ind. Japan, 12, 258 (1956);
Ohsugi, T., Matsumoto, M., Tanabe, K., and Ohno, K. (Kurashiki Rayon Co.), BP 745,219.

[7] Mori, N., Tanaka, T., Sakurai, K., and Nakamura, N., J. Soc. Textile Cellulose Ind. Japan., 12, 76, 245 (1956).

[8] Tanabe, K., Ohno, K., and Takeshima, K., ibid., 10, 172 (1954);
Tomonari, T., Ohsugi, T., Tanabe, K., and Ohno, K. (Kurashiki Rayon Co.), BP 732,934.

[9] Sakurada, I., Yamamoto, A., Yasutake, T., and Tsuji, W., Ann. Rep. Japan Inst. Chem. Fibres, 10, 55 (1954).

[10] Tanabe, K., and Ohno, K., J. Soc. Textile Cellulose Ind. Japan, 12, 543 (1956); BP 732,934.

[11] Sakurada, I., Yamamoto, A., and Sakaguchi, Y., Kobunshi-Tembo, 6, 59 (1952).

[12] Ohsugi, T., Tanabe, K., and Ohno, K. (Kurashiki Rayon Co.), BP 733,102.

[13] Ohsugi, T., Tanabe, K., Ohno, K., and Suda, T. (Kurashiki Rayon Co.), BP Application No. 36,665 (1955).

[14] Sakurada, I., Chem. High Polymers (Japan), 12, 302, 308, 311 (1955).

Discussion

Mr. H. R. HADFIELD: Since you state that phenol results in improved dyeability, I wonder whether carrier dyeing is used commercially in Japan for dyeing vinylon.

Mr. NOMURA: No, carrier dyeing is not used in Japan for vinylon. Some carriers have been tried, including 2-hydroxydiphenyl and benzoic acid, but the results have always proved unattractive commercially.

Mr. HADFIELD: Does vinylon require setting before dyeing, and can materials made from vinylon be given a permanent pleat?

Mr. NOMURA: Vinylon has a thermoplastic behaviour intermediate between those of cotton and cellulose acetate. Therefore heat-setting before dyeing is not required. If vinylon materials require permanent pleating, a thermoplastic resin must be applied first.

Dr. T. VICKERSTAFF: Is the reduction in dye uptake at high degrees of formalisation due to a rate effect, for all the dyeings were carried out for 1 hr. only?

Mr. TANABE: It may be, but even for longer dyeing times the further increase of dye uptake at high degrees of formalisation may be small, and our conclusion may not be very different.

Dr. VICKERSTAFF: Can reactive dyes be applied to vinylon or basified vinylon?

Mr. TANABE: Procion (ICI) dyes showed only poor dyeing effects for formalised vinylon, but very good dyeing effects for animalised vinylon.

Dr. D. PATTERSON: Have you any estimates of the percentage crystallinity of vinylon fibres? The figures quoted for the specific gravity of the fibres in Table II seem to suggest that during processing the crystallinity does not increase very much.

Mr. TANABE: Professor I. Sakurada in Japan has estimated the percentage crystallinity of polyvinyl alcohol fibres by an X-ray method, and finds a value of 66% with an ordinary vinylon [14]. It is impossible to estimate the crystallinity from the values for the specific gravity in Table II, because these vinylon fibres have a hollow space in the core, e.g. as shown in Fig. 13.

Dr. P. SCHLACK: How is the light fastness of dyeings with acid dyes influenced by animalisation? Does any cumulative adverse effect arise from combinations of acetal groups and amino groups?

Mr. TANABE: We have not found that the light fastness of dyeings of animalised vinylon with acid dyes is influenced by the combination of acetal groups and amino groups.

Dr. SCHLACK: Is the light fastness of dyeings of vinylon influenced by the type of aldehyde used for hardening?

Mr. TANABE: There is no great difference in light fastness under normal conditions between formalised vinylon and benzalised vinylon. We have not examined the light fastness of dyeings of vinylon acetalised with other aldehydes.

The Application of Reactive Dyes to Viscose Rayon

J. A. FOWLER and C. PRESTON

Reactive dyes of the Procion type* offer a versatile dyeing system for producing dyeings of attractive colour and good fastness to washing. A merit of the Procion system is that, since it is based on a simple chemical reaction with the fibre, it is capable of variation in easily controlled and readily understood ways common to many chemical reactions. The rate of the fixation reaction can be made to vary from slow at room temperature and mild alkalinity to rapid at high temperature or high alkalinity, intermediate rates being achievable at will by controlling various simple factors. Choice of method of dyeing is therefore wide and will depend largely on the particular equipment readily available.

In the search for new dyes which is being pursued with ever increasing vigour as markets expand and competition intensifies, the emphasis hitherto has been largely on the ultimate properties of the dyed material. Ease of application and flexibility in the dyeing conditions are, however, of very obvious importance, despite the fact that all recent tendencies have been, of necessity, towards the use of more specialised machinery and more complicated dyeing methods.

With conventional dyes improved quality of performance demands some complication of dyeing technique, whereas it is one of the virtues of reactive dyes that dyeings with outstanding properties can be obtained by a variety of techniques over a wide range of conditions. The theoretical reasons for the advantages to be obtained by the use of reactive dyes have been outlined by Vickerstaff [1].

Although aimed at for many years, the target of a simple and commercially acceptable means of achieving the chemical linkage of a water-soluble dye to cellulose proved elusive until the discovery of the Procion dyes*. It is with these dyes that the present paper is concerned. Except where specifically stated otherwise, the term *Procion dyes* here refers to "cold-dyeing" Procion types and not to H brands.

Procion dyes are water-soluble and contain a reactive group capable of linking with cellulose, particularly under alkaline conditions. The structure of a Procion dye may be represented as S–R–X, where S represents one or more sulphonic-acid groups conferring solubility on the molecule, R the coloured organic molecule, and X a reactive halogen atom. The reaction between Procion dye and cellulose may therefore be represented as follows—

$$S \cdot R \cdot X + HO \cdot Cellulose \longrightarrow S \cdot R \cdot O \cdot Cellulose + HX$$

Since the reaction takes place from aqueous solution, it would appear inevitable that a side-reaction with water would also go forward, as follows—

$$S \cdot R \cdot X + HOH \longrightarrow S \cdot R \cdot OH + HX$$

The reaction with cellulose appears, however, to be surprisingly rapid compared with the side-

Patents applied for in most industrial countries.

reaction, and it is this feature of the system that transforms these reactive dyes from an interesting academic curiosity to the basis of a new and commercially attractive dyeing system. Equally important is the fact that preferential reaction with the cellulose takes place even at ordinary room temperature and also persists at temperatures well above 100°C. This, combined with the small size of the molecules of the dyes, which allows relatively rapid diffusion in viscose rayon even at low temperatures, means that Procion dyes provide an extremely flexible dyeing system, in that dyeing can now be carried out in reasonable dyeing times at all temperatures from room temperature (or below) to above the boil.

In addition, further flexibility is imparted by the fact that reaction with viscose rayon is very greatly accelerated by the presence of alkali, whilst being negligibly slow under neutral conditions. This allows the dye to be adsorbed on to viscose rayon in an unreacted state in the same way as direct dyes are adsorbed, with the difference, of course, that the affinity is, in general, markedly lower. The importance of this property is twofold. In the first place, when the dyes are used for batch processing, they may be applied in a controlled and level manner in neutral solution by the addition of salt before the second stage of bringing about reaction by the addition of alkali. Secondly, since reaction in presence of alkali takes place not only with cellulose but also with water, it is of obvious advantage that a proportion of the dye should be already *in situ* in the fibre ready for reaction; in this way reaction with the fibre rather than with the water is favoured. If dyes of this kind are to be used both for batch dyeing and also for application by continuous padding methods, there must clearly be a limit set to the affinity of the dyes in the unreacted state. If affinity were too high, difficulty might arise from unlevelness and poor penetration, and such a dye would not be suitable for continuous processing, since tailing would occur. Although Procion dyes somewhat vary in neutral affinity from member to member, they are in general of the low-affinity type.

In summary, therefore, Procion dyes, because of their high reactivity for cellulose in presence of alkali and their low molecular weight and low affinity in neutral solution, may be dyed on to

viscose rayon over a wide temperature range including room temperature, and both by batchwise processes and by continuous methods. The various dyeing procedures will now be outlined.

(I) Cold Batchwise Dyeing

Batchwise dyeing at room temperature is best carried out by omitting alkali from the dyebath in the early stages for the reason mentioned earlier, namely that if an initial period is allowed during which the dye is adsorbed on the fibre, to some extent, in the unreacted state, a higher degree of fixation is achieved when alkali is subsequently added. After about half-an-hour a suitable alkali is added, and dyeing continued for a further period of $1-1\frac{1}{2}$ hr. During this period of fixation side-reaction with water also occurs, and an unreactive hydroxy derivative of the dye is formed; this will, in the presence of salt,

Affinity
──────── 50 g. NaCl per litre
    pH   Exhaustion
  10·3 ── ── ── +2·0 g. Na$_2$CO$_3$ per litre
  10·1 ── ── ── +1·0 g. Na$_2$CO$_3$ per litre
   9·8 ············ +0·5 g. Na$_2$CO$_3$ per litre
   9·3 ──·──·── +0·2 g. Na$_2$CO$_3$ per litre
  ° Fixation after scouring in Lissapol NC (2 g./litre)

FIG. 1— Effect of Concentration of Sodium Carbonate (1·5% Procion Blue 3GS on viscose rayon in a 30:1 liquor at 20°C.)

have some affinity for the fibre, but this loose dye may readily be removed by scouring.

It has already been mentioned that Procion dyes differ somewhat in neutral affinity, from member to member. Similarly, although the two effects by no means go hand in hand, the reactivity for cellulose and for water differ somewhat from dye to dye. This is made apparent if we consider the effect of alkalinity of the dyebath upon the fixation of the various dyes. This has been determined at room temperature by dyeing hanks of viscose rayon under standard conditions, which include a 30:1 liquor ratio and a total dyeing time of 2 hr. The dyes were applied in 1·5% depth, and the baths were made alkaline after running for 30 min. under neutral salt conditions. The course of a typical dyeing is shown in Fig. 1. Each dye was studied over a range of dyebath pH values, achieved by adding alkalis of differing strength at a concentration of 2 g./litre.

Fig. 2 and 3 show that, under the conditions outlined, there is, for each dye, an optimum range of alkalinity. Below this optimum, reaction with both fibre and water is relatively slow; above this range, the reaction rate is markedly increased, and it can be deduced that the effect of excess alkalinity is to influence the reaction with water preferentially. If this is so, then it would be expected that for dyeing times longer than 2 hr. the optimum pH would fall, and there is evidence that this is so, although the time required is long and the improvement in degree of fixation not very significant.

With regard to the various values of the optimum pH for the different dyes, it is seen that Procion Brilliant Red 2B and, to a less extent, Procion Brilliant Red 5B and Procion Blue 3G have unusually low values, but the remaining dyes have similar reactivity.

With mixtures of dyes the pH chosen should, of course, be a compromise between the individual values for the separate components. Since soda ash, even in the presence of 50 g. of common salt
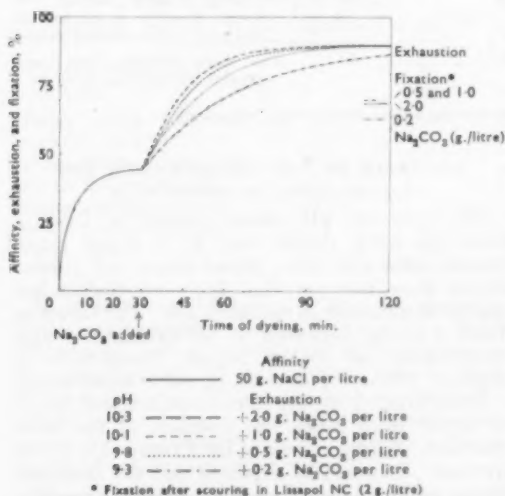

──────── 20°C.
── ── ── 30°C.

(i) Procion Brilliant Orange GS
(ii) Procion Blue 3GS
(iii) Procion Brilliant Yellow 6GS

(iv) Procion Yellow RS
(v) Procion Brilliant Blue RS
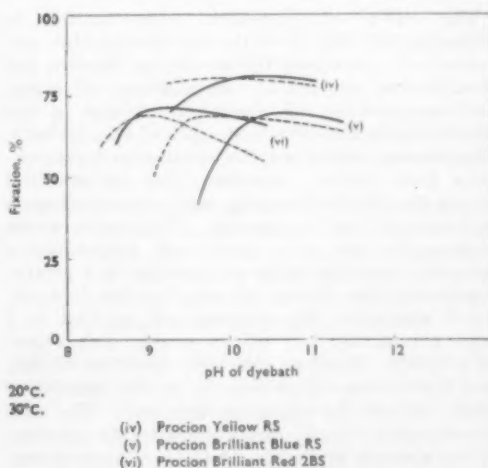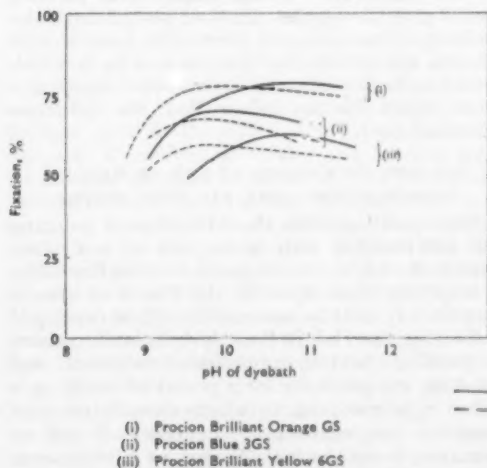(vi) Procion Brilliant Red 2BS

FIG. 2 and 3— Effect of pH on the Fixation of Procion Dyes on Viscose Rayon (1·5% dye in 30:1 liquor containing 50 g. salt + 2 g. alkali per litre)

TABLE I

Dyeing Properties of Cold-dyeing Procion Dyes on Viscose Rayon

Procion Dye (1·5%)	Optimum pH for Dyeing	Exhaustion·(%)* with		Fixation* (%)	Comment
		Salt (50 g./litre)	Salt (50 g./litre) + Soda (1·5 g./litre)		
Brilliant Yellow 6GS	10·5	34	71	61	Moderate affinity in long liquors; a more level-dyeing shading component than Procion Yellow R
Yellow RS	10·3–10·6	78	99	81	High exhaustion with salt alone indicates that care should be taken to obtain an even strike
Brilliant Orange GS	10·5–11·0	53	98	77	High tinctorial value and excellent building up
Brilliant Red 2BS	9·3	35	86	68	The preferred red component for mixture dyeings
Brilliant Red 5BS	9·6	51	95	73	Particularly suitable for deep reds in view of its superior building-up properties and tinctorial value compared with Procion Brilliant Red 2B
Brilliant Blue RS	10·6	11	90	67	In deep colours raising the temp. to 40°c. is advised at the end of the dyeing period
Blue 3GS	10·0	43	92	69	The more suitable blue component for mixture dyeings

* Liquor ratio 30 : 1 at 20°c.; total dyeing time 120 min. (30 min. without alkali, 90 min. with alkali).

per litre, can give a pH of 10·3, it is a suitable alkali for the dyeing of viscose rayon. With those dyes which require a slightly higher pH for optimum fixation at 20°c., it may be preferable to raise the temperature, say to about 25°c., rather than to use a stronger alkali. Such a rise in temperature, by speeding up the reaction with the fibre, has an effect similar to a slight rise in pH.

The values of optimum pH quoted in Table I refer to experiments in which the salt concentration was held at 50 g./litre. For pale dyeings such a high concentration might prove uneconomical, and it is therefore necessary to consider the effect of salt concentration on optimum pH.

EFFECT OF SALT CONCENTRATION ON OPTIMUM pH

The effect of electrolyte concentration in enhancing the affinity of the dye for the fibre and therefore in increasing the percentage fixation has already been referred to. In addition, of course, the concentration of electrolyte present in the alkaline bath also affects the pH of the dyebath. Experiments over a range of electrolyte concentrations have shown, however, that in practical dyeing the effect of varying salt concentration on optimum pH can be ignored. This comes about because the use of a lower salt concentration not only allows the alkali to dissociate to a greater extent and thus gives a higher pH to the dyebath, but it also raises the optimum pH, so that to a large extent the two effects cancel each other. In practice, therefore, the concentration of salt used has no important bearing on the amount of alkali needed for optimum fixation. The salt concentration, clearly, has a considerable influence on the fixation of Procion dyes on viscose rayon, but this is due to the well recognised effect of increasing affinity already mentioned.

INFLUENCE OF DYE CONCENTRATION AND LIQUOR RATIO ON OPTIMUM pH

The optimum pH values quoted in Table I relate to 1·5% depth and 30:1 liquor ratio. Experiments with lower liquor ratios and greater depths show, however, that dye concentration has negligible influence on optimum pH. The values in Table I apply, therefore, to all dyeings at room temperature on viscose rayon, irrespective of depth of colour, liquor ratio, or salt concentration.

Consideration of dye concentration and hence of liquor ratio raises the question of the side-reaction— the hydrolysis of the Procion dye in the dyebath. It would be expected that the lower the liquor ratio the less important this side-reaction would be, and this is, in fact, the case. Carried to the limit, this would imply that padding would give the highest fixation; and, indeed, the padding of viscose rayon fabric with a solution of Procion dye followed by fixation in a jig or winch set with alkaline salt solution at room temperature gives higher fixation values than the technique described above.

PADDING TECHNIQUES AT LOW OR MEDIUM TEMPERATURES— THE PAD–ROLL SYSTEM

Since padding offers the advantage of reducing the side-reaction with water and since Procion dyes fix readily at low temperatures, the feasibility of applying these dyes by the Pad–Roll system immediately calls for assessment. First developed in Sweden, the Pad–Roll method, in brief, consists in padding, heating by infrared radiation, and batching up, generally for a period of hours, on a roller in a container in which temperature and humidity are controlled. In effect, if not in principle, it can be looked upon as a continuous process. It is normally used for dyeing with direct dyes, and it is apparent that dyeing with Procion

dyes on this system offers problems for solution, since, although the method visualised for Procions — padding cold, heating, and batching up— is fundamentally the same as that developed for direct dyes, the temperature used and the dyebath both require special consideration.

With regard to dyebath stability, it is apparent that if the dyebath is held at the optimum pH found for cold batch-dyeing, the side-reaction with water will occur in the padding trough throughout the run, leading eventually to a weaker dyeing. This effect would, of course, be largely offset by using a small padding trough and by adding dye and alkali continuously at appropriate rates. Nevertheless, a technique of this kind would be unattractive if the stability of the padding liquor were very severely limited.

TABLE II
Dyebath Stability at 20°C.

(Minimum time (hr.) to show significant change in dyebath efficiency)

Dyebath concn., g./litre	5	20
pH value	8	9·4
Procion Brilliant Yellow 6G	6	5
Procion Yellow R	6+	5
Procion Brilliant Orange G	6	5
Procion Brilliant Red 2B	4	1
Procion Brilliant Red 5B	6	3
Procion Brilliant Blue R	6	5
Procion Blue 3G	6	2–3

In order to test dyebath stability, viscose rayon fabrics were padded through dye solutions at different pH values immediately after addition of dye, and batched for a length of time to give optimum fixation. This was repeated at intervals of time as the dyebath aged. Table II shows the results for dyebaths producing pale to medium depths of colour on viscose rayon.

These figures show that in sodium bicarbonate solutions, at pH 8, Procion Brilliant Red 2B (the most unstable of these dyes), at a concentration of 5 g./litre, has a bath life of 4 hr. At pH 9·4, obtained with a mixture of sodium carbonate and sodium bicarbonate, the bath life of this dye at 20 g./litre is reduced to 1 hr., whilst the remainder are stable for much longer; even with Procion Brilliant Red 2B the stability would probably be adequate if mechanical mixing and feeding into the padding trough were provided. At pH 8 good fixation occurs from a 5 g./litre padding liquor in a batching time at 20°c. of 24 hr. Under these conditions, for example, Procion Brilliant Red 2B, Procion Yellow R, and Procion Blue 3G show fixations of over 80%. With medium depths and a 20 g./litre padding liquor at pH 9·6, maximum fixation takes place in 2 hr. with Procion Brilliant Red 2B, Procion Brilliant Red 5B, and Procion Blue 3G, and in 5 hr. with the remaining dyes in Table II. The fixation is again over 80%. Since the Pad–Roll system has been designed to allow for relatively long dyeing times (if necessary up to 6 hr.), it would seem that this system is feasible for cold dyeing with Procion dyes at pH about 9·4.

It is apparent, however, that the difficulty associated with instability of the padding liquor may in some cases be a deterrent. It is illustrative of the versatility of Procion dyes that this difficulty may be surmounted in two ways whilst still retaining the Pad–Roll system.

The first of these, which has already been mentioned and which may require an uneconomically long batching time, is to take advantage of the fact that the alkalinity of sodium bicarbonate solution is sufficient to promote the Procion reaction with viscose rayon even at room temperature. The reaction at the low pH of sodium bicarbonate solution is, as would be expected, extremely slow, and at pH 8 Procion Yellow R requires an even longer batching time, at medium depths, than the 24 hr. required for Procion Brilliant Red 2B and Procion Blue 3G.

However, an alternative to lengthening the time is to raise the temperature. Since the fixation of Procion dyes involves a chemical reaction, its rate is markedly increased by a rise in temperature. For example, at 50°c., with all these dyes, maximum fixation is achieved, in pale colours, in a batching time of 15–30 min., sodium bicarbonate being used as alkali.

With 5% dyeings on viscose rayon, times for maximum fixation are longer, ranging from 1 hr. for Procion Brilliant Red 2B to 6 hr. for Procion Yellow R. Such times are, of course, appropriate to a Pad–Roll process, and this system therefore allows dyeings with Procion dyes to be made using moderate temperatures, reasonably short fixation times, and relatively stable dyebaths.

(II) Continuous Dyeing

It has so far been shown that Procion dyes can be applied satisfactorily in the following ways—

(1) Under conditions of very mild alkalinity (e.g. from solutions of sodium bicarbonate) at room temperature, a long dyeing time is essential and, because of differences in reactivity from dye to dye, very long dyeing times would be generally required if mixtures of dyes were to be applied.

(2) By increasing the alkalinity to the optimum pH for the single dye or a compromise pH (sodium carbonate) for a mixture, dyeings can be made at 20°c. in as short a time as 1½–2 hr.

(3) Under conditions of very mild alkalinity (sodium bicarbonate) by padding through cold solutions and raising the temperature of the fabric, after padding, to 50°c. dyeings can be carried out in a time suitable for the Pad–Roll system.

These results indicate that a rapid and continuous method of dyeing can be arrived at by either (a) using a padding technique employing very strong alkali at room temperature or (b) increasing the rate of fixation by heating the cloth impregnated with alkaline dye liquor to a high temperature.

The first alternative is made unattractive by the rapid decomposition of dye which takes place in strong alkali at room temperature.

The second, however, provides an elegant method of applying Procion dyes. This takes advantage of the facts that dye solutions are stable for long periods of time in sodium bicarbonate solution and that when a cloth, impregnated with sodium bicarbonate solution, is heated to the region of 100°c. the stronger alkali, sodium carbonate, is formed, which is sufficiently alkaline to produce fixation of the whole range of Procion dyes in a matter of seconds or minutes, according to the heating conditions. In the work described below, the heat-treatment was carried out in a laboratory oven with the fabric held vertically on stenter frames inserted through slits in the oven roof. This allowed patterns to be placed in the oven without any very considerable initial drop in air temperature.

FIG. 4— Effect of Duration of Heat-treatment (at 130°c.) on Fixation of Procion Brilliant Yellow 6G (40 g./litre) on Spun Viscose Rayon Staple

The effects of several variables are discussed below.

DURATION OF HEAT-TREATMENT

Early experiments showed that the degree of fixation achieved by this bicarbonate-pad–heat system is markedly influenced by the drying or baking conditions, particularly for heavy depths. For instance, in some cases the degree of fixation differs considerably if the pattern is air-dried before entering the high-temperature atmosphere rather than if entered whilst still wet. In general, the higher fixation was achieved if the pattern was wet. In addition, a considerable enhancement of fixation was found when even a relatively small quantity of steam was passed into the oven during treatment. The volume of the oven was 170 litres and steam was passed in at the rate of 6 g./min. Experiments were performed to follow the change in fixation of dye with time both with and without the addition of steam to the oven.

Typical curves (Fig. 4) show that, not only does presence of steam increase the fixation, but it also increases the rate of fixation. The enhanced fixation in presence of steam is shown by all the Procion dyes other than Procion Brilliant Red 2B and Procion Blue 3G. Typical figures are given in Table III.

The reason for this improvement in fixation in presence of steam is not completely understood, and it is clear that this technically very simple dyeing procedure involves the interplay of a number of factors. An important function of the steam is probably to assist the transfer of heat from the heated oven surfaces to the cloth, thus accelerating the rise in temperature of the cloth; latent-heat effects may also play a considerable part in the early stages of the heating treatment. Further, it must be borne in mind that the presence of steam will retard the rate of drying of the cloth, and since it is improbable that the Procion reaction will occur under dry conditions, this reduction in drying rate is likely to be a beneficial factor. Indeed, it is always found that, for a given time and temperature, optimum fixation (except in the case of Procion Brilliant Red 2B) is obtained with a steam input which leaves the cloth slightly damp to the touch at the end of the fixation. Since the side-reaction with water also occurs to some extent even on padded
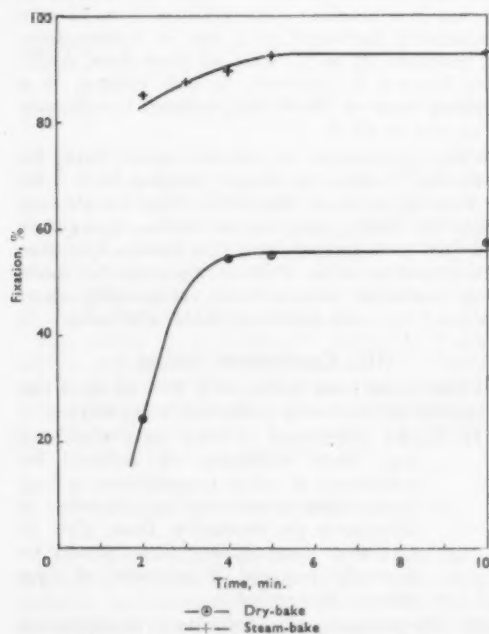
TABLE III

Minimum Times* required (in Laboratory Oven) for Maximum Fixation by Dry Heat and by Steam Heat at 130°C.

(Sodium bicarbonate concentration 10 g./litre)

Procion Dye	Dye Concn. in Padding Liquor (g./litre)	Minimum Time required for Max. Fixation (min.)		Fixation (%)	
		Dry	Steam	Dry	Steam
Brilliant Yellow 6G	40	3	3	55	90
Yellow R	40	4	3	60	90
Brilliant Orange G	30	4	2	62	83
Brilliant Red 2B	40	2	1	70	80
Brilliant Red 5B	30	3	2	72	75
Brilliant Blue R	40	3	2	35	75
Blue 3G	40	4	1	80	80

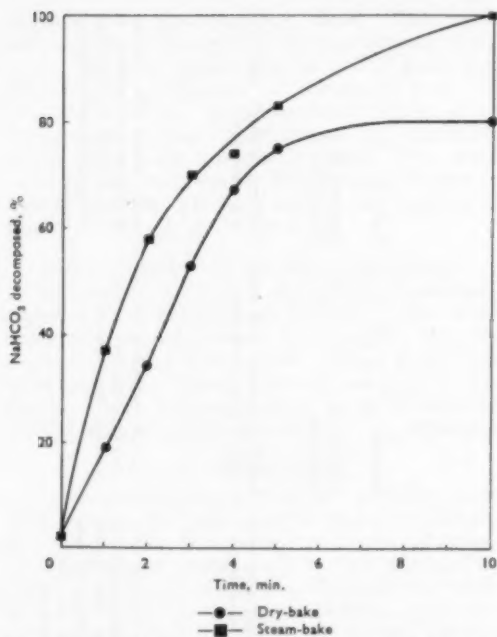* In bulk processing some variation from these times may be necessary.

FIG. 5— Decomposition of Sodium Bicarbonate (10 g./litre) on Bleached Cotton (liquor take-up 100% on weight of fabric) during Baking at 105°C.
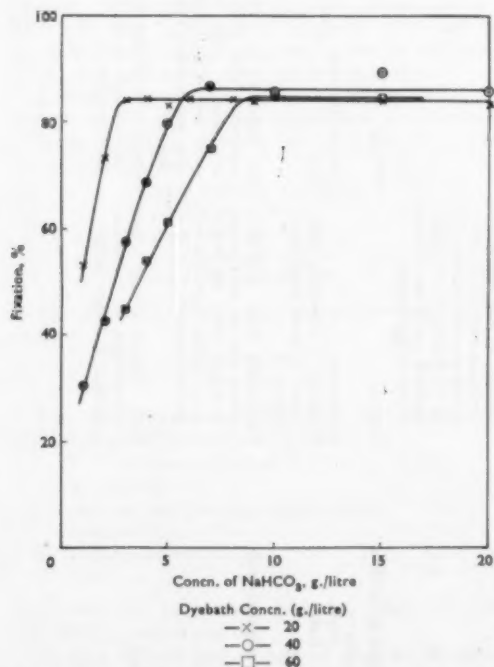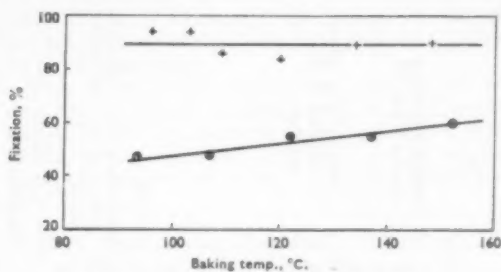
— ● — Dry-bake   — ■ — Steam-bake
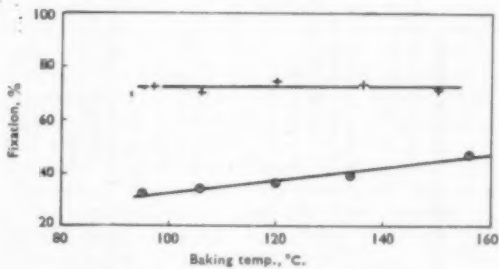

FIG. 7— Procion Brilliant Yellow 6G (30 g./litre)

FIG. 8— Procion Brilliant Blue R (40 g./litre)
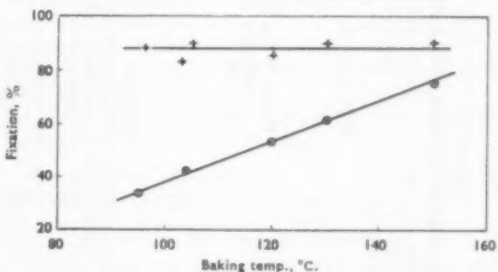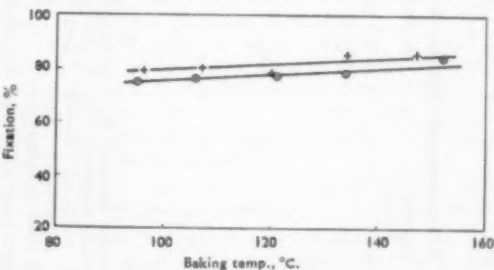

FIG. 9— Procion Yellow RS (40 g./litre)

FIG. 10— Procion Brilliant Red 2BS (40 g./litre)

—○— Dry-bake   —+— Steam-bake

FIG. 7–10— Effect of Baking Temperature on Fixation of Procion Dyes on Light Spun Viscose Rayon Staple

Dyebath Concn. (g./litre)
— × — 20
— ○ — 40
— □ — 60

FIG. 6— Effect of Concentration of Sodium Bicarbonate on Fixation of Procion Brilliant Red 2BS on Spun Viscose Rayon Staple

cloth, and since this side-reaction will, like the dye–cellulose reaction, be enhanced by temperature, it can be envisaged that by increasing the water available (by steam treatment) a slight loss in fixation is feasible, and this appears to be the case with Procion Brilliant Red 2B. It will be remembered also that cold-dyeing experiments discussed earlier showed that Procion Brilliant Red 2B had a lower optimum pH value for the

TABLE IV

Comparison of Different Methods of applying Cold-dyeing Procion Dyes to Viscose Rayon

	Batchwise Dyeing	Pad(bicarbonate)–Batch–Wash off (Pad–Roll Process)	Pad(bicarbonate)–Dry–Wash off	Pad(bicarbonate–urea)–Dry–Wash off	Pad(bicarbonate)–Steam–Wash off
Depth of colour obtainable	All	All	Pale–medium	Necessary only for full colours; otherwise pad (bicarbonate)–dry process recommended	Procion Blue 3G not suitable in deep colours
Dyes which are suitable	All	All	Yellow R and Brilliant Blue R suitable only in pale colours	All, but maximum improvement with— Brilliant Yellow 6G Yellow R Brilliant Orange G Brilliant Red 5B Brilliant Blue R	
Use in mixtures	Suitable	Suitable	Suitable	Suitable	Suitable
Colour matching and reproducibility	Satisfactory provided that careful control over dye-bath conditions (especially temperature and liquor ratio) is exercised	Determined by mechanical efficiency of the plant used	Determined by mechanical efficiency of the plant used	Determined by mechanical efficiency of the plant used	Determined by mechanical efficiency of the plant used
Penetration and levelness	In general very good, but not suitable for dense or tightly woven materials (unless a pad-jig or pad-winch process is adopted) or for multi-ply or highly twisted yarns in certain types of equipment	Excellent	Excellent	Excellent	Excellent
Fastness properties	Normal	Normal	Normal	Normal	Normal
Production— (a) Form (b) Rate	Batchwise Moderate— especially suitable for small weights of material	Semi-continuous High	Continuous Very high	Continuous Very high	Continuous Very high
Plant requirements	Practically any available plant can be used satisfactorily (but see comment under "penetration and levelness")	For piece-goods, ideally operated with Pad–Roll equipment, but where cold batching is carried out no special requirements	Padding mangle and suitable drying equipment	Padding mangle and suitable drying equipment	Padding mangle and 1–2 min. steamer
General	Cold batch-dyeing has advantages in potential savings in steam usage	Permits the production of fast dyeings on the Pad-Roll machine	Can be run in tandem with a resin finishing range, in which case the intermediate washing-off and drying may be omitted with pale colours	A useful extension of the pad(bicarbonate)–dry process for deep colours	Useful where the drying equipment available is not suitable for operating the pad(bicarbonate)–dry process

dyebath than the remaining dyes. This factor undoubtedly plays a part in the phenomenon under discussion, since experiment showed (Fig. 5) that the rate of production of carbonate from bicarbonate during heat-treatment of a cloth impregnated with bicarbonate is markedly accelerated by the presence of steam. This effect could, presumably, favour the fixation of dyes of higher optimum pH and reduce the fixation of Procion Brilliant Red 2B.

CONCENTRATION OF SODIUM BICARBONATE

The minimum amount of sodium bicarbonate required to give maximum fixation under these conditions ranged from 2 to 10 g./litre for dye concentrations of 2–60 g./litre. Using more than these amounts of bicarbonate did not improve the fixation. Fig. 6 shows typical curves of fixation plotted against sodium bicarbonate concentration.

DRYING TEMPERATURE

Temperatures ranging from 95° to 150°c. have been studied. In this range the degree of fixation on viscose rayon is not very markedly influenced by temperature, particularly in the presence of steam. Fig. 7–10, which also illustrate the effect of injection of steam upon fixation, show the temperature effect for a number of dyes applied to light-weight viscose rayon staple fabric.

ADDITION OF UREA TO THE PADDING LIQUOR

It has been found that, if urea is added to the padding liquors in relatively large quantity (150–200 g./litre), an increased tinctorial yield can be obtained in the pad-bicarbonate–dry process, particularly at high dye concentrations. This effect is particularly striking with cotton, but is less so with viscose rayon, where the efficiency of the reaction is in any case much higher.

A worthwhile increase in tinctorial yield in heavy depths on viscose rayon can be obtained with the following dyes by the addition of urea to the padding bath—

> Procion Brilliant Yellow 6G
> Procion Yellow R
> Procion Brilliant Orange G
> Procion Brilliant Red 5B
> Procion Brilliant Blue R

In the case of the following, there is no increase in yield—

> Procion Brilliant Red 2B
> Procion Blue 3G

For the purposes of operating the process in bulk, a typical recipe is as follows—

PADDING LIQUOR	g./litre
Procion dye	*x*
Common salt (as migration inhibitor)	10
Lissapol N	2
Sodium bicarbonate	10
Urea	200

Pad cold at maximum pick-up, then dry at 100–120°c., and wash off.

By this means deeper colours can be obtained than are possible by using the normal pad-(bicarbonate)–dry process in the absence of urea, but with the same advantages in respect of ease of processing; in addition, the urea process requires no additional plant.

It is worth noting that, whilst the amount of urea required seems relatively large, the additional cost of processing due to the urea addition is only of the order of ¼d. per yard for a normal-weight cloth at the present United Kingdom price for urea.

(III) Application of Padding Techniques to Materials other than Piece-goods

So far the application of padding methods has been discussed only in relation to piece-goods; these padding techniques, i.e. the pad–batch, pad–dry, and pad–steam processes, can also be adopted in practice for the dyeing of a number of other types of material, e.g. tufted viscose rayon carpets, loose viscose rayon staple, viscose rayon tow and warps.

Loose viscose rayon staple fibre lends itself particularly well to this treatment. A suggested *modus operandi* is to pass the fibre through an impregnating solution containing Procion dye, wetting agent, and sodium bicarbonate, the fibre being carried along on a suitable inert cloth (e.g. one constructed from Terylene polyester fibre) or on a metal brattice. The material is then squeezed, and may be allowed to lie to enable fixation of the Procion dye to occur. Alternatively, the fibre may be dried at 100–120°c. to obtain fixation of the dye. In either case, the fibre is finally scoured in the normal way to remove unfixed dye.

For purposes of reference, the various dyeing methods are compared in Table IV.

(IV) Procion H Brands

So far, this discussion has been limited to the so-called "cold-dyeing" Procion dyes, and no mention has been made of the Procion H brands such as Procion Brilliant Red H3B.

These are reactive dyes capable of giving on cellulosic fibres, colorations of similar brilliance and fastness to those obtained with the cold-dyeing Procion dyes. They are, however, less reactive than the cold-dyeing types, and differ from them in two important respects—

> (i) They are not recommended for cold batchwise application to cellulosic fibres
>
> (ii) They are unsuitable in general for the normal pad(bicarbonate)–dry technique discussed in this paper.

Because of their lower reactivity, the H brands in general require the use of stronger alkalis and higher temperatures than are recommended with the cold-dyeing brands, and for these reasons the dyeing methods must be suitably modified.

DYEHOUSE DEPARTMENT
    IMPERIAL CHEMICAL INDUSTRIES LTD.
      DYESTUFFS DIVISION
        HEXAGON HOUSE
          MANCHESTER 9

Reference

[1] Vickerstaff, T., *J.S.D.C.*, **73**, 237 (1957).

Discussion

Mr. G. S. A. CORBISHLEY: What suggestions can you offer for improving the distribution of dye between viscose rayon and cotton in union fabrics, e.g. a fabric with cotton warp and rayon staple weft, both in continuous dyeing by the pad-bicarbonate method and in batch dyeing on the jig? The use of sodium phosphate does not seem particularly successful, especially with Procion Brilliant Blue R.

Mr. FOWLER: The question of solidity of colour between the two fibres in cotton–viscose rayon unions is currently receiving our attention. I agree that the use of trisodium phosphate makes less improvement than might be expected, but I would expect good solidity to be obtained by the normal pad(bicarbonate)–dry method.

Mr. C. P. ATKINSON: As regards the continuous procedure for fixation after padding, could Mr. Fowler confirm that a suitably modified hot-flue type of drier, on the lines indicated, without subsequent steaming and followed by a continuous washing-off range, would be adequate for the purpose?

Mr. FOWLER: On the basis of our laboratory experiments, a hot-flue type of drier, suitably modified, represents a satisfactory method of fixing Procion dyes on cellulosic fibres. For maximum fixation, together with minimum migration, the hot flue should preferably be a three-stage type: the first compartment should be relatively cool, and the cloth should be dried down to 30–40% moisture by the end of the second compartment, after which it is only necessary in the final compartment to maintain this humidity at a temperature of 100–105°c. to complete fixation.

Mr. J. GREENWOOD: The method of boiling acid hydrolysis has been recommended for the partial stripping of goods which have been too heavily dyed with reactive dyes. Are any other methods of reduction available which do not destroy the colour for subsequent redyeing with reactive dyes?

Mr. FOWLER: I regret that, whilst we have examined this problem, the methods already suggested, partial stripping by acid hydrolysis or complete colour destruction by means of oxidising or reducing agents, are the only suitable ones.

Mr. GREENWOOD: Reactive dyes have been introduced into industry in various styles, so that we now have samples for identification which may have been produced with such dyes. Is there any systematic scheme of identification, or have we to proceed by a process of elimination?

Mr. W. G. HARLAND: An earlier speaker asked for methods of identifying Procion dyes on fabrics. It has been reported that cellulose is not completely soluble in cuprammonium hydroxide after it has been dyed or printed with Procion dyes. Would this form a satisfactory basis for the detection of Procion dyes on cotton or rayon to which no resin finish has been applied?

Mr. FOWLER: It would not be entirely satisfactory, since the solubility or otherwise of Procion-dyed fabrics depends upon the method by which they have been dyed, and also on the depth of colour. Suggested tests from which pointers can be obtained are—

(a) Extraction with boiling water, which will indicate a "fast colour".

(b) Extraction with solvents, e.g. pyridine, which has no effect on Procion dyes, but which will partially or completely strip other classes of dyes, such as direct, vat, and azoic.

(c) Reduction with sodium hydrosulphite followed by diazotisation and development with an azoic coupling component, e.g. Brenthol FO. With certain reactive dyes of the azo type, a part of the dye molecule remains attached to the fibre and resists washing out, so that it can be developed to a coloured substance. The process can be repeated indefinitely.

Dr. W. FURNESS: I should like to ask whether the increased tinctorial yield obtainable in the presence of urea is realised in dyeing at room temperature or only at elevated temperatures. If the tinctorial yield is improved only at high temperatures, may this effect be due to slight hydrolysis of urea, as a result of which the pH of the dyeing liquor is raised, or is this effect specific for urea? If it were possible to show that the improvement in tinctorial yield is a consequence of or is coincident with a rise in pH, perhaps it would be possible to produce a similar effect more easily, cheaply, and at lower temperatures by substituting ammonium bicarbonate for urea in the padding liquor.

Mr. FOWLER: The increased tinctorial yield in the presence of urea is realised only at elevated temperatures. The effect does not appear to be associated with decomposition of urea, nor has ammonium bicarbonate been found to be an effective substitute for urea.

Mr. J. G. G. GRANT: In the literature issued so far on the reactive dyes, little attention has been paid to their application to viscose rayon yarns. I am referring principally to the bulk dyeing of spun rayon staple in a pressure machine packed in hank form. Would Mr. Fowler care to comment on this?

Mr. FOWLER: We have not had very much success in the application of Procion dyes to filament viscose rayon cakes, but I see no reason why there should be any real difficulty in their application to all other forms of viscose rayon package dyeing. I suggest that packed hanks in a circulating-liquor machine might occasion a little more difficulty than, for instance, cheese dyeing, but this is really a matter of the correct packing of the hanks, together with the normal precautions taken in package dyeing generally.

Mr. T. KALINOWSKI: Why is such a long time of batching recommended in the cold Pad–Roll dyeing method, when the reaction of Procion dyes with cellulose is said to be instantaneous in the presence of soda ash?

Mr. FOWLER: The reaction with cellulose is indeed instantaneous, and long times are recommended in the cold-dyeing processes in order to allow diffusion of the dye within the cellulose prior to reaction. Where soda ash is used cold, the time

of dyeing is 1–2 hr. for both batch and Pad–Roll methods; with cold sodium bicarbonate, the time of dyeing is very much longer, and may be as long as 24 hr.

Mr. KALINOWSKI: What is the light fastness of spun viscose rayon staple dyed with 0·04 of the standard depth of (*a*) Procion Brilliant Red 5BS, (*b*) Procion Brilliant Blue H7GS and crease-resist-finished with urea–formaldehyde resin, ammonium phosphate being used as catalyst in both cases ?

Mr. FOWLER: The light fastness of (*a*) Procion Brilliant Red 5BS at 0·04 standard depth on spun viscose rayon is 5 (straight) and 3–4 (urea–form-aldehyde-finished). With (*b*) Procion Brilliant Blue H7GS at standard depth the comparable figures are 6–7 and 4–5, but with urea–formaldehyde, and ammonium phosphate, chloride, or thiocyanate as catalyst, the dyeings are phototropic and turn violet temporarily. This effect is not shown if magnesium or zinc chloride is used as the catalyst, provided that the goods are washed off.

Mr. H. BELLIS: Could we produce a good white cellulose acetate reserve on a deep turquoise on an acetate–viscose rayon cloth?

Mr. FOWLER: Procion Brilliant Blue H7GS is not particularly suitable for producing cellulose acetate reserve effects and is inferior in this respect to the "cold-dyeing" types, presumably because the former is applied hot and in the presence of stronger alkali.

Mr. H. W. PARTRIDGE: In dyeing greys with mixtures of Procions Yellow RS, Blue 3GS, and Brilliant Red 2BS, we encountered difficulty owing to the different dyeing properties and lower resistance to clearing of the Yellow RS. Can you recommend a more suitable mixture of Procion dyes for producing such colours?

Mr. FOWLER: In this case, Procion Brilliant Orange GS would be a more suitable yellow component than Procion Yellow RS. In any case, for greys it is essential to control the dyeing conditions, particularly the temperature and the liquor ratio, if reproducibility is to be maintained from batch to batch.

Dr. G. H. LISTER: Since these dyes react with proteins as well as cellulosic fibres, is there any possibility of pathological effects, and are any special precautions required in handling powders and solutions?

Mr. FOWLER: It is not necessary to take any special precautions other than those normally taken when dealing with dyes as fine powders. We have not encountered any difficulty in this respect to date, either in the manufacture of the dyes or in their use.

Mr. D. HAIGH: Viscose rayon warp–cotton weft galloons are notoriously difficult to penetrate with the faster direct or metal-complex dyes. Preliminary experiments with Procion dyes did not prove very satisfactory, as penetration was still inadequate. Would the authors recommend the use of the Pad–Roll system or any other padding system for dyeing such narrow, tightly woven fabrics?

Mr. FOWLER: Padding methods in general give more satisfactory results in respect of levelness and solidity of colour than do batch-dyeing methods. Of the padding methods, I would expect the Pad–Roll technique to give the best result, although I have no experience of the technique as applied to hat galloons.

COLLOQUIUM ON HIGH-TEMPERATURE DYEING

Chairman— Mr. CLIFFORD PAINE

The High-temperature Dyeing of Terylene Slubbing or Loose Stock

FRED SMITH

Practical aspects of the operation of machines designed for dyeing loose fibres at temperatures above the boil are discussed, special stress being laid on safety precautions.

INTRODUCTION

The mechanics of the application of dyes to fibres is as important as the rate of dyeing of a single fibre, particularly with dyes that are not self-levelling.

Dyeing at temperatures above that attainable at normal atmospheric pressure has enabled fibres to be dyed satisfactorily, which could otherwise be dyed only with difficulty and in some cases not at all in the conventional machines available.
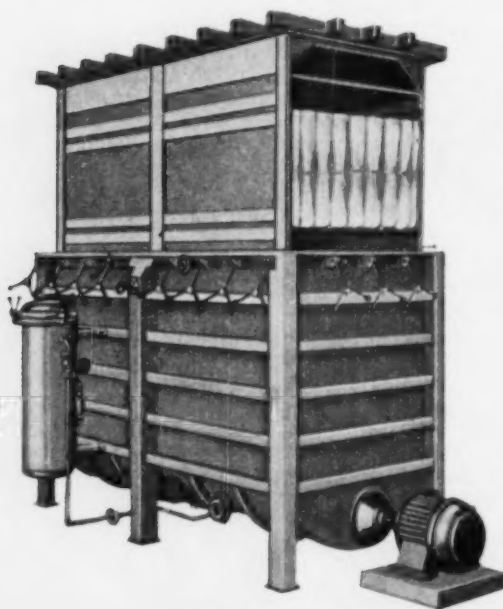
FIG. 1— Scholl Skein Dyer

The design of the conventional machine used for package dyeing did not need much alteration for use with high temperatures, and it was with this type of machine that most of the early work was done. Subsequently, machines have been developed for piece goods, i.e. the Barotor (DuP), totally enclosed jiggers, and the star frame. Recently, a machine for dyeing in hank form was introduced by Scholl (Fig. 1). The difficulty of piece dyeing on the winch is that the pieces get entangled, although I think that it will be possible to design a machine that will prevent this and enable pieces to be dyed at high temperatures in rope form.

As this is one of four short papers of a colloquium, it will be confined to the mechanics of the application of dyes, in the hope that it may prove useful to students and those not already acquainted with the mechanical side of dyeing at high temperatures.

The application of high temperatures to any already existing system for the application of dyes requires a suitably enclosed machine, designed and made of material strong enough to withstand safely a pressure sufficiently high to enable the required temperature to be reached with a margin of safety, satisfying the Board of Trade regulations governing enclosed vessels used for pressures above atmospheric. These require safety valves on any vessel or part of a machine which may have to be separately sealed off from the atmosphere at any time during the operation of dyeing, storing of liquor or heat exchange device, where a separate exchange is installed. Just as one insures a steam-generating plant, which is subject to periodic inspection, when certificates are issued giving the maximum working pressure allowed without risk of severe consequential loss, so one should insure any high-temperature dyeing machine.

The hydraulic pressure created by the pump in circulating the liquor is not in itself dangerous, but when added to the static pressure it could be sufficient to exceed the weight any part of the machine is designed to stand, causing it to fracture and release the static pressure with a violent explosion. It is having to build to withstand these internal stresses which makes these machines much more costly than ordinary dyeing machines.

Whether a machine is to dye loose fibres, yarn in cheese, cone, cake or hank, sliver in either ball or bump form or reeled into hank, the body of the machine has the same shape. The design of the container or material carriers is different, to suit whatever form is to be dyed.

Sampling devices vary somewhat with different makes of machine and should be so placed and designed as to give the same rate of flow passing through the sample pot as through the bulk. The sample should be weighed out in direct ratio to the

bulk and packed to the same density, otherwise the rate of flow is bound to be different. If care is taken to work this out properly, then the colour of the sample will represent that of the bulk satisfactorily; if not, there will be fairly wide differences in colour, because many dyes have lower affinity at top temperature, and on cooling down more dye will be taken up. This may apply to one dye more than to another, causing a variation in hue as well as depth.

In some machines the hot liquor can be drawn away from the goods, and the machine opened and the goods examined. If they are satisfactory, the

THE STEVERLYNCK AND OBERMAIER SYSTEMS

The Steverlynck machine has a special cylinder into which compressed air can be blown, by which static pressure can be applied at low temperatures. Whilst this is not necessary with high temperatures, which build up their own static pressure, it has the advantage of preventing a void at the suction side of the pump when the temperature is approximately at the boil, particularly when the pack is fairly dense, which may slow down the full flow of the pump. This air tank is also a very successful device for making additions at high temperature.
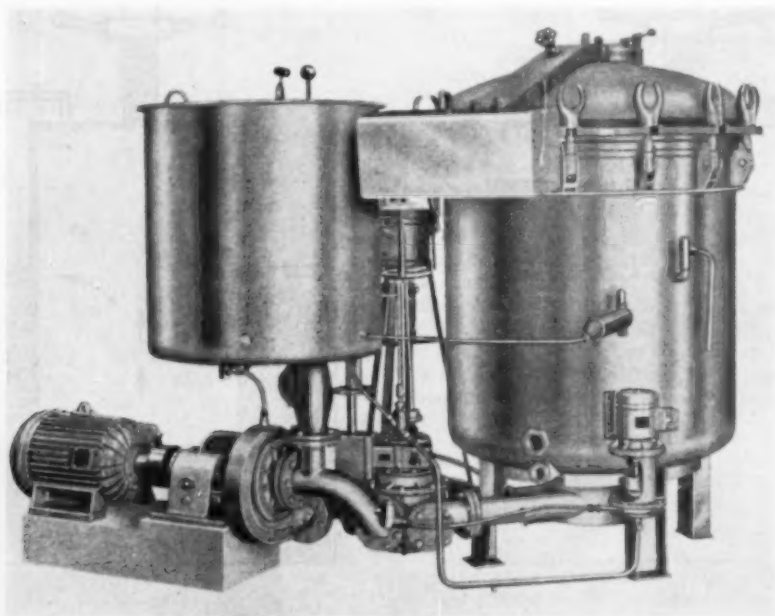
FIG. 2— Obermaier Machine with Special Cooling System

machine can be cooled down without returning the unexhausted liquor. This tends to give somewhat cleaner dyeings, though at the expense of dye.

Other machines cannot be opened before cooling down below static pressure, and in order to have the sample and bulk in the same condition, the whole system has to be cooled, unless from experience one can estimate the difference from the sample taken hot, in which case, if any additions have to be made, the whole system must be reheated. I would suggest that the makers fit a sampling device with a small pump, so that the liquor in the sample pot can be circulated whilst it is cooling down; this would save considerable time and expense. [A]

MAKING ADDITIONS AT TOP TEMPERATURE

This needs a special closed vessel which can be sealed off from the closed circuit, evacuated, and opened up for necessary additions to be made. The vessel is then closed again, and the circuit opened, allowing the addition to percolate into the main or closed auxiliary tank.

Obermaier uses a different system for preventing a void in the suction, which also allows an open expansion tank where the state of the liquor can be examined and additions can be made at any time without interrupting the process, in the same manner as can be done in low-temperature machines. This, however, entails the fitting of a separately driven small pump, which draws a certain amount of high-temperature liquor which has been forced through a cooling system into the open expansion tank at a temperature low enough to be forced by this pump into the main suction pipe close to the main pump. This is claimed to prevent a void, and the amount of cooling in the main tank is negligible (Fig. 2).

This machine also has fitted a separate cooling system to the sample tank with its own thermometer. This boosting and sampling method is worthy of mention, as I consider it unique in principle. Other machine makers all fit effective systems for making additions and sampling.

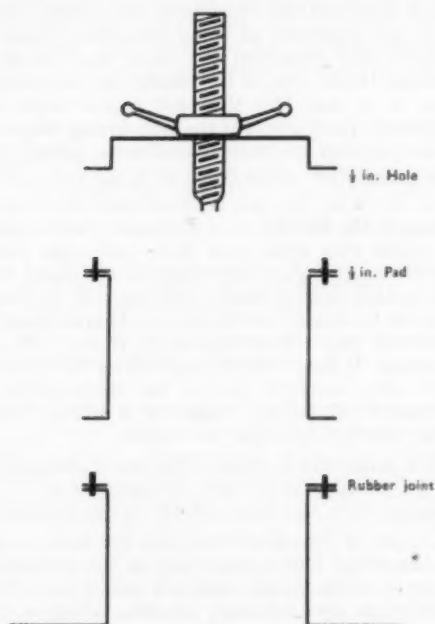In my opinion there is room for simplification of

design, which could very well reduce the high cost of these high-temperature machines without lowering their efficiency.

AUTOMATIC CONTROLS

Whilst these are not essential and are expensive, they are useful where one man is minding a number of machines.

There are automatic controls on the market which can be set to heat up to a given temperature at a predetermined rate and time, hold at that temperature for a set time, make a record chart for future reference, give a warning signal at the finish

run off. Before further treatment is given, the space left by sinkage will require taking up by further tightening the nut on the screw which holds down the bonnet. If this is not done, trouble may arise in any subsequent treatment (see Fig. 3).

A certain amount of reswelling of the shrunken pack takes place with the entry of the second bath, which must take place slowly so as not to disturb the pack. After the reswelling has taken place is the time to adjust the bonnet screw. Reswelling allows the liquor to percolate more evenly into the pack. If the liquor is allowed to enter with full force before the bonnet is fast in contact with the

FIG. 3— Method of Packing (capacity 200 lb. of Terylene; scale ⅜ in. ≃ 1 ft.)

of the cycle, and at the same time alternate the direction of flow with equal or varying times for each direction as may be desired. These control fittings add considerable cost to the plant and its upkeep, and whilst they are not essential, they are desirable if of a reliable make. Otherwise, they can be more trouble than they are worth. It is, however, my recommendation that, where the full gamut of automatic controls is not fitted, some automatic control of temperature is most essential.

There are many makers of machines suitable for high-temperature dyeing, and any particular make is mentioned here only if it has some special feature which has come to my knowledge and which may be different from the general principle. Whether it be of any advantage or not must be judged by the user.

PACKING

The best package density I have found to be 10 lb. to the cubic foot of dyeing space when in the dry state. This after wetting and dyeing will shrink approx. 10%, or a little more when the liquor has

pack, there is liable to be a blow-out. When the machine is loaded to its capacity at the right density, the bonnet, if properly designed, will be deep enough for any shrinkage to be taken up right through the many processes simply by adjustment of the screw. It is possible to pack at a lower density when smaller weights are required, by opening up the material and letting the bonnet sit firmly on top without screwing down too far; the liquor is then allowed to enter slowly with the pump running and the inlet valve just sufficiently opened to allow this. No shrinkage takes place with the pump running; and it is only slight if the liquor level is as high as the pack with the pump stopped. In the case of a less dense pack a greater gap is left between the plate and the bonnet, which may not be taken up by reswelling or if the bonnet is not deep enough. Should it be necessary to use a second bath, this space will need to be filled either by waste material or by having a spare bonnet sufficiently deep. A good idea is to have a bonnet with spare distance rings on it (Fig. 4). These are only necessary for

¼ in. Hole

¼ in. Pad

Rubber joint

FIG. 4

this or a similar type of cylinder with horizontal flow. With machines having vertical flow, sometimes used for loose fibre, they are not necessary.

In a container similar to that of Fig. 3 one can dye satisfactorily loose fibre, top reeled into hanks or in bump form, and yarn in hank form with dyes suitable for package dyeing (in the same machine with different material carriers). Fibres in top form can be dyed by mounting them on separate perforated tubes, as well as yarns suitably wound on cone or cheese. The density of packing of yarn spun from fibres can vary from 10 lb. per cubic foot for fine single yarns to 15 lb. for twofold yarns, because a single yarn offers more resistance to flow.

Processing with Azoic and Disperse Dyes

It is well known that at high temperatures these products are in a much finer state, nearer to true solution, than at low temperatures, and as exhaustion in many cases is not complete [1, 2], the liquor will contain a considerable amount of unexhausted dye, which must be run off at as high a temperature as possible in order to avoid any dye precipitating on the fibre as a result of cooling down too low. It is only necessary to cool to 200°F. before the machine can be safely opened for inspection, unless the liquor can be forced back into the closed expansion tank and sealed off, when all that is necessary is to open the air vent and release any live steam left in the dyeing compartment. Any water passed through the cooling system should be
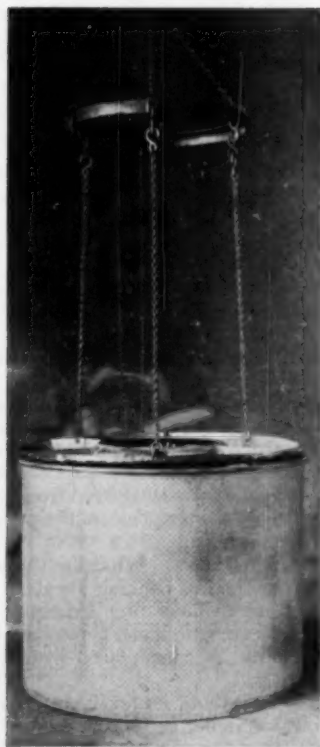
FIG. 5 and 6— Arrangement for unloading Obermaier Machine

piped into the hot-water storage tank, thus saving water and heat.

UNLOADING LOOSE OR HAND-PACKED SLUBBING

Unless the outer perforated cylinder is separately fitted to the bottom plate so that it can be lifted clear of the material, it will be difficult to unpack, especially with loose fibre. Fig. 5 and 6 show a chain-and-plate system for lifting out the material and transferring it to the hydroextractor.

The advantages of the high-temperature dyeing of man-made fibres are, with Terylene —

Use of a disperse black with C.I. Azoic Coupling Component 18 in one bath plus diazotisation, as against a disperse black with Brentosyn BB (ICI), at high temperature using two baths, or at 100°C. using carriers with two baths and diazotisation. The first method gives a cleaner black at less cost in dyes and time. Dyeing with disperse dyes of the highest fastness at high temperature gives deeper and cleaner dyeings with less dye than can be obtained by the use of carriers at 100°C. for the same colour. Good repetition of colour, better levelling, and saving of dyeing time are other advantages[3].

Finally, more long and tedious work is necessary on exhaustion rates of the component parts of the azoic dyeings, when applied together, in order to give the best and most economical final shade, though I am sure that the dyemakers are giving this their attention.

GENERAL REMARKS

Once the right conditions of packing and working have been established and good results obtained, and the machine is kept in good condition, it will not cause variation in itself. There are, however, other variables, such as low steam pressure, bad packing, entering at different temperatures, causing time variations in raising or lowering the temperature, bad thermometers giving false readings, and faulty automatic temperature control. If the time at the desired temperature necessary for a dye to be transferred into the fibre is not given, a darker and duller colour will result

which is not so fast to rubbing or scouring. Also, with dye mixtures, as some dyes take longer to exhaust and penetrate the fibre than others, a different colour will be the result. An experienced dyer in a case like this will realise what has happened, particularly if the first dyeing was done under properly controlled conditions, giving optimum tinctorial value from each dye.

If, however, the temperature and the time of dyeing in the first lot were such as to yield a colour in which two dyes gave their optimum values while the third gave less than the optimum, then the second dyeing done correctly will be heavy towards the hue of this third dye. This fault can be corrected only by stripping or boiling off and redyeing. If the faulty dyeing follows the correctly dyed one, however, raising the temperature or continued processing, whichever is wrong, should make the dyeings equal in colour.

It is a mistake to make additions of shading dye before making sure that optimum results are obtained from the dyes already in the machine.

Control of the pH of water and dye liquor is also an important factor, especially in the application of azoic combinations and 3:2-hydroxynaphthoic acid. Some dyes are more sensitive to liquor ratio than others, and some adjustment is necessary if this varies to any extent.

One cannot stress too strongly the possible dangers in the use of high-temperature machinery, due to the build-up of static pressure. The machine minder must be properly instructed not to attempt to loosen the holding nuts or open the machine until the temperature is down to 200°F. and the air valve open to release any live steam, or he may be badly scalded.

WM. SMITH & CO. LTD.
CLIFFE DYE WORKS
BRUNTCLIFFE
NEAR LEEDS

References

[1] Fern, A. S., J.S.D.C., **71**, 502 (1955).
[2] Fern, A. S., and Hadfield, H. R., ibid., **71**, 840 (1955).
[3] See Fern, A. S., ibid., **71**, 510 (1955).

Discussion

Dr. J. F. GAUNT: Reference is made in the paper to simplification in design which might reduce the high cost of high-temperature dyeing machines without impairing their efficiency. Would the lecturer recommend omitting the use of automatic controls, or eliminating the reserve tank and cooling the liquor by passing cold water through the heating coil?

Mr. SMITH: I was not referring to automatic controls, as these are not essential, though I should always fit a temperature control as a safety measure. In my opinion the simplest form would be one kier with heating and cooling coil built in, plus the open expansion tank for starting up and finishing without losing any liquor, as I do not use the air pressure tank when dyeing at high temperature, since the rise in temperature develops its

own pressure. This also is not necessary, although it is very useful for dyeing at temperatures up to the boil with the top valve open to allow overflow into the open expansion tank, particularly when tightly packed goods are being dyed from outside to inside, as without the air pressure the pump would then lose its efficiency.

Mr. H. R. HADFIELD[*]: What are the lecturer's views on the method of packing Terylene tops for high-temperature dyeing? For example, does he prefer packing in an Obermaier type of cage, or does he prefer dyeing as tops placed over a central spindle?

Mr. SMITH[*]: I would prefer dyeing tops placed over a central spindle, as in this system there is a much smaller radius of material for the liquor to

* Communicated.

pass through; this enables the dye to be put more easily where it is required, giving more level results with dyes that do not equalise easily. Further, with packing in an Obermaier type of cage with a narrow race, much of the dyeing space is taken up by the wide centre column and the deep lid necessary for sealing, but this space can be utilised by dyeing on the spindle system.

The High-temperature Disperse Dyeing of Terylene Polyester Fibre

H. R. HADFIELD and R. BROADHURST

The building-up and the levelling properties on Terylene of a fast and a slowly diffusing disperse dye have been compared over the temperature range 85–140°c. Both properties improve rapidly as the temperature of the dyebath is raised above 100°c. Optimum dyeing conditions are attained between 120° and 130°c., and optimum levelling conditions between 130° and 140°c. Under high-temperature dyeing conditions the slowly diffusing dye gives the better dyebath exhaustion and the rapidly diffusing dye has the better levelling properties.

A considerable amount of work has been published on the dyeing behaviour of Terylene above 100°c.[1-4]. Fern[4] compared in detail the dyeing behaviour of a number of Dispersol and Duranol dyes, applied to Terylene at 100°c. with *o*-phenylphenol as a carrier and at 120°c. without a carrier. Other variables studied by Fern were the effects of dyebath pH and time of dyeing. A comparison was also made of the levelling behaviour of disperse dyes at 100°c. with no carrier, at 100°c. with a carrier, and at 120°c. without a carrier. This work clearly demonstrated the beneficial result of high-temperature dyeing. As greater experience of the requirements for dyes for Terylene was accumulated, it became clear that the rapidly diffusing dyes were of less value than the slowly diffusing disperse dyes, for the latter type possessed higher fastness to heat-treatments such as pleating processes[5]. It was therefore decided to extend the work of Fern to include a study of the effect of dyeing Terylene over a temperature range of 85–140°c. and to compare in detail the building-up and the levelling properties of a fast and a slowly diffusing dye over the above range of temperatures.

Experimental

MATERIALS

YARN— Bright ordinary-tenacity continuous-filament Terylene yarn (65-denier/33-filament) was used.

DYES AND AUXILIARY PRODUCTS—Commercially available brands were used.

DYEING APPARATUS

All dyeings and levelling tests were carried out in a rotating dyeing machine capable of dyeing 1–5-g. hanks of yarn at all temperatures up to 140°c. The design of the apparatus has been fully described by Graham and Jamin[6].

DYEING METHODS

BUILD-UP TESTS— The yarn (2 g.) was dyed for 1 hr. at the required temperature in 80 ml. of dye liquor containing 0·08 g. of Lissapol C Paste and the appropriate quantity of dye.

LEVELLING TESTS— Dyed and undyed yarn (2 g. each) were treated at the appropriate temperature for 1 hr. in 80 ml. of liquor containing 0·08 g. of Lissapol C Paste.

CLEARING TREATMENTS— Before estimation of the dye absorbed by the fibre, the dyed yarn was treated for 20 min. at 50°c. in 100 ml. of a solution containing 0·2 g. of caustic soda, 0·2 g. of sodium hydrosulphite, and 0·2 g. of Lissolamine A 50%. The process was concluded by treating for 15 min. at 50°c. in 100 ml. of a solution containing 0·2 g. of Lissapol N and finally rinsing in cold water.

ESTIMATION OF DYE

Weighed samples of the dry dyed yarn were dissolved in *o*-chlorophenol, and the amount of dye present was determined from optical-density measurements using a Spekker photoelectric absorptiometer.

Results and Discussion

Two dyes were selected for the detailed examination. Dispersol Fast Orange G (C.I. Disperse Orange 3) was chosen as a rapidly diffusing dye which is relatively easy to build-up to heavy depths and which possesses poor fastness to heat-treatments. Dispersol Fast Orange B (C.I. Disperse Orange 13) was chosen as a slowly diffusing dye which is more difficult to build-up to heavy depths but which is very fast to heat-treatments. The tinctorial strength of Dispersol Fast Orange B is one-third of that of Dispersol Fast Orange G, and therefore, as the practical dyer is concerned ultimately with tinctorial yield, this strength relationship must constantly be borne in mind in interpreting the results.

Fig. 1 and 2 illustrate the "building-up" isotherms obtained by measuring the amount of dye absorbed by the fibre with different amounts of dye added to the dyebath. The practical dyer is not generally required to produce dyeings on Terylene containing more than 10% of Dispersol Fast Orange B 300 or 3·3% of Dispersol Fast Orange G 300. In the case of Dispersol Fast Orange G 300 it will be seen that, practically, there is little gain in exhaustion in using a temperature higher than 115°c.; but in the extreme case, beyond the depth normally of interest to the practical dyer, increased exhaustion is obtained as the temperature of dyeing is raised to 140°c. In the case of Dispersol Fast Orange B 300 it will be seen that a dyeing temperature of 130°c. is necessary to obtain the heavier depths of practical importance. Below
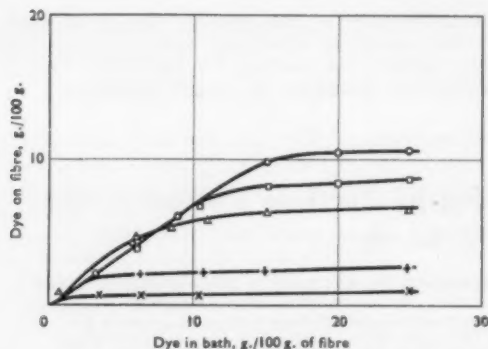
FIG. 1—Dispersol Fast Orange G 300 Powder Fine
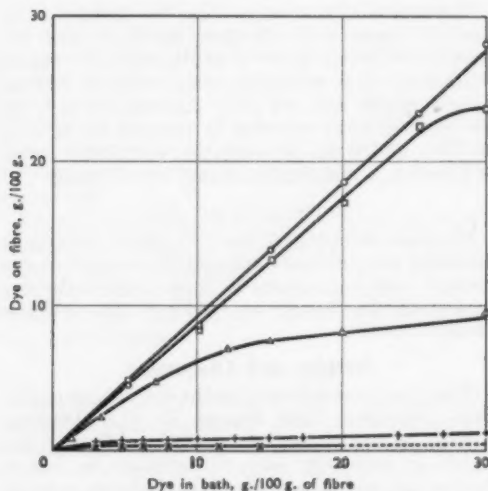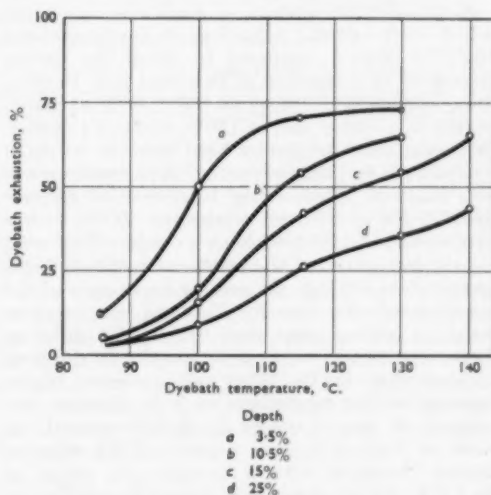(C.I. Disperse Orange 3)

FIG. 2— Dispersol Fast Orange B 300 Powder Fine
(C.I. Disperse Orange 13)

Dyebath Temperature
○ —— 140°C.
□ —— 130°C.
△ —— 115°C.
+ —— 100°C.
× —— 85°C.

FIG. 1 and 2— Effect of Dyebath Temperature on Building-up
Properties

130°c. apparent saturation of the fibre is obtained at, very approximately, an 8·0% depth.

It will be appreciated that the apparent saturation of the fibre obtained by dyeing at the lower temperatures results from a saturation of the surface of the fibre by dye, and that, in practical dyeing times, only a limited quantity of dye can diffuse, from the surface layer, into the fibre. An increase in the dyeing temperature results in an increase in the rate of diffusion, and therefore raises the quantity of dye absorbed in a given practical dyeing time.

The results given in Fig. 1 and 2 have been used to illustrate the effect of an increase in the dyeing temperature upon the dyebath exhaustion. It will be seen from Fig. 3 and 4 that, for the heaviest dyeings studied, the exhaustion is still increasing

as the temperature of dyeing is increased up to 140°c., which was the maximum temperature employed. The results in Fig. 3 and 4 clearly illustrate the difference in dyeing behaviour between the fast and the slowly diffusing disperse dyes. With 3·5% Dispersol Fast Orange G 300 (the rapidly diffusing dye) there is a rapid improvement in exhaustion between 90° and 110°c., but with 15% Dispersol Fast Orange B 300 (slowly diffusing) a similar improvement in exhaustion is not obtained until a temperature of 110°c. is exceeded. In addition, the results in Fig. 3 and 4 show clearly that, in order to obtain satisfactory exhaustion of Dispersol Fast Orange B in heavy depths, the dyeing temperature must be increased to 130°c. Thus, with 7·0% Dispersol Fast Orange B 300 an exhaustion of 75% is obtained at 116°c.,

Depth
a　3·5%
b　10·5%
c　15%
d　25%

FIG. 3— Dispersol Fast Orange G 300 Powder Fine
(C.I. Disperse Orange 3)

Depth
a　7%
b　15%
c　20%
d　30%
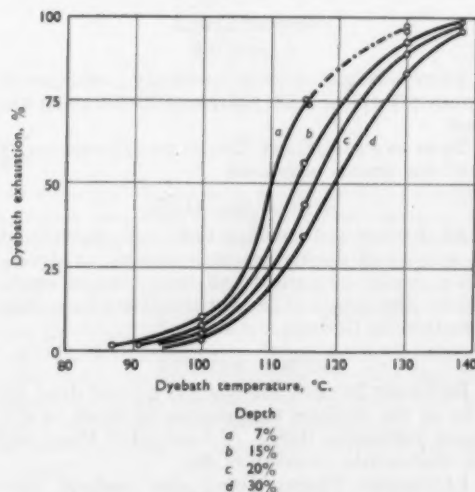
FIG. 4— Dispersol Fast Orange B 300 Powder Fine
(C.I. Disperse Orange 13)

FIG. 3 and 4— Effect of Dyebath Temperature on Exhaustion

SANDOZ

Finish NSW

non-slip agent
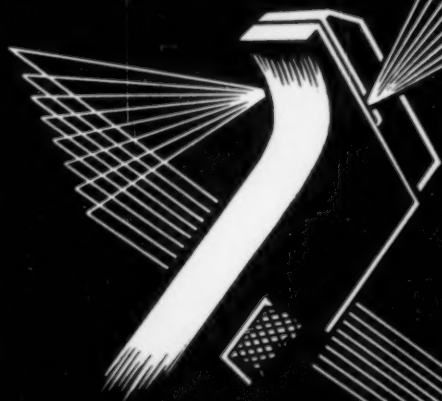
for rayon, rayon mixtures and man-made textiles. Considerably increases the adhesion of warp and weft, giving a full and firm handle.

SANDOZ PRODUCTS LTD. BRADFORD

face centre

°Cibacron dyes in textile printing

Cibacron dyes

are suitable for roller and screen printing

can be applied from various types of thickening

give print pastes of unlimited stability

can be fixed by steam or dry heat

do not clog the engravings on printing rollers

are virtually unaffected by crushing

are suitable for

direct printing

printing alongside practically all classes of dyes

resists under Aniline Black, Cibantine pad dyeings and Fast Blue VB Salt

discharge and resist printing

Cibacron dyes – novel, fast, and brilliant – a true chemical bond links dye with cellulosic fibre.

CIBA Limited, Basle, Switzerland
The Clayton Dyestuffs Co. Ltd., Manchester,
Sole Concessionaires in the United Kingdom

® Registered Trade Mark.

CIBA

AZONINE

AND

DURANTINE

DYESTUFFS

FOR

COTTON

TOWN END

Town End Chemical Works Limited

BRAMLEY LEEDS

───○─── 3% Dispersol Fast Orange G 300 (C.I. Disperse Orange 3)
───×─── 9% Dispersol Fast Orange B 300 (C.I. Disperse Orange 13)
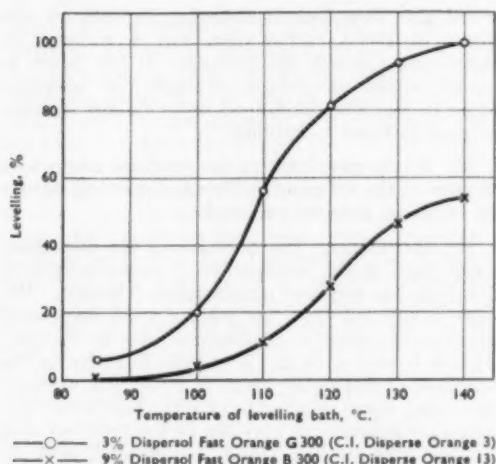
FIG. 5—Effect of Dyebath Temperature on Levelling

but with 30% of dye a temperature of 130°c. is required to produce the same exhaustion.

Fig. 5 shows the effect of temperature upon levelling. The rapidly diffusing dye (Dispersol Fast Orange G) shows more levelling at all temperatures than the slowly diffusing but fast-to-heat dye (Dispersol Fast Orange B). Good levelling is obtained at 120–130°c. with the former, but the levelling of the latter dye is only moderate at 130°c., and is not significantly improved by raising the temperature to 140°c. Further improvement is not possible, as the high-temperature dyeing machines at present available to the trade do not generally allow for dyeing at temperatures greater than 130°c. In addition, as the dyeing temperature

is increased the risk of fibre degradation is also increased, and for the above two reasons it is suggested that 130°c. represents the preferred dyeing temperature for the high-temperature dyeing of Terylene.

Conclusions

1. In the application of heavy depths of disperse dyes to Terylene the dyebath exhaustion is increased as the temperature is raised to 140°c. There is a marked improvement on increasing the dyeing temperature from 120°c. to 130°c.

2. The improvement in yield as the dyeing temperature is raised above 120°c. is higher with slowly diffusing dyes than with rapidly diffusing dyes.

3. There is a very significant improvement in levelling as the dyeing temperature is increased up to 140°c. Even at the highest temperature studied the slowly diffusing dyes show inferior levelling compared with the rapidly diffusing dyes.

4. For the dyeing of Terylene, as a compromise between the dyeing properties of the dye, the mechanical properties of the dyeing machines available, and properties of the fibre, a temperature of 130°c. is suggested as the optimum.

DYEHOUSE DEPARTMENT
    IMPERIAL CHEMICAL INDUSTRIES LTD.
        DYESTUFFS DIVISION
            HEXAGON HOUSE
                MANCHESTER 9

References

[1] Roy, Amer. Dyestuff Rep., **41**, 35, 844 (1952).
[2] Reith and Andres, ibid., **42**, P 35 (1953).
[3] ICI, BP 698,490.
[4] Fern, J.S.D.C., **71**, 502 (1955).
[5] Fern and Hadfield, ibid., **71**, 840 (1955).
[6] Graham and Jamin, Hexagon Digest, No. 24, 19 (1956).

Discussion

Dr. G. H. LISTER: Most of the work has been carried out with single dyes. Is there any danger of mixed-melting-point phenomena occurring when mixtures, particularly yellows, oranges, and reds, are applied at 130°c.? Such effects have been known to occur, resulting in tar formation accompanying the application of mixtures of disperse dyes even at lower temperatures.

Mr. HADFIELD: We agree that depression of melting point in mixtures of disperse dyes is a possible cause of unsatisfactory results. With the dyes currently recommended for Terylene, however, there is no danger of this phenomenon occurring. As a general rule, disperse dyes with a low melting point should be avoided for the dyeing of Terylene, a suggested minimum being 140°c.

Mr. R. K. FOURNESS: Experiment has confirmed that certain dyes giving rise to tarring trouble at temperatures of, say, 80°c. can be successfully applied at 120–130°c.

Mr. HADFIELD: We can envisage the possibility that a dye which melts at a low temperature such as 80°c. and tars could give a good result at 120–130°c., providing that the particular dye was extremely soluble in the dispersing agent at the

higher temperature. We still consider, however, that dyes which melt under the conditions of dyeing are to be avoided whenever possible in the high-temperature dyeing of Terylene.

Dr. LISTER: Instances have been known with disperse dyes on secondary cellulose acetate in which a heavy wine or maroon dyeing showed satisfactory fastness to rubbing at the dyeing temperature and on the cloth immediately after leaving the driers. On cooling to room temperature, however, inferior rubbing fastness developed, owing to crystallisation of the disperse dye at the lower temperature. Are such phenomena more likely to occur as a result of the high-temperature dyeing of Terylene in deep colours?

Mr. HADFIELD: We are aware of a particular disperse dye which is very soluble in aqueous solutions of the dispersing agents and which can, as a result, crystallise on the surface of the fabric and result in poor rubbing fastness. This dye is not of value for Terylene. With all disperse dyes there will be an increased tendency for this defect to occur, owing to their greater solubility at 130°c. compared with the commercial boil. In practice, however, no serious difficulties, which could be traced to crystallisation of the disperse dye on the

fibre surface, result with the preferred dyes for Terylene.

Mr. W. H. JONES: Fig. 3 appears to confirm my suspicions that with Terylene there is a point at which a disperse dye saturates the fibre at a particular temperature; e.g. 3·5% Dispersol Fast Orange G 300 shows a higher tinctorial value than a greater depth of the same dye.

Mr. HADFIELD: The fact that, at a given temperature, each disperse dye has an apparent saturation point cannot be stressed sufficiently. In practical dyeing, if attempts are made to build up beyond this apparent saturation point, then the extra dye added to the bath merely results in precipitation on the fibre surface.

Mr. H. W. PARTRIDGE: Is the behaviour of disperse dyes at 130°c. in agreement with the suggestion that they are in true solution at that temperature?

Mr. HADFIELD: The behaviour of disperse dyes at 130°c. is in agreement with the suggestion that a high proportion of the dye is dissolved in the aqueous solution of the dispersing agent. Thus, for example, slow cooling of the dye liquor from 130° to 60°c. can, in certain cases, result in formation of comparatively large crystals of dye. To avoid this behaviour it is better to blow off the liquor at 130°c. rather than cool it whilst it is circulating through the package. If the liquor is cooled whilst circulating through the package, there is a greater likelihood of producing dyeings of poor fastness to rubbing.

Mr. FOURNESS: Have the authors made any studies of the effect of different dispersing agents on levelling, exhaustion, etc.?

Mr. HADFIELD: The question of the dispersing agent used in the application of disperse dyes to Terylene has received considerable attention. We have concluded that, no matter what dispersing agent is employed, a compromise must be effected. That is to say, each dye is specific in so far as the selection of dispersing agent is concerned, and the dispersing agent selected to give the best behaviour with one disperse dye may not be the most suitable if other dyes are being used. No detailed work on the effect of dispersing agents on the levelling or exhaustion properties of the disperse dyes applied to Terylene has been carried out. Our work with dispersing agents has been undertaken primarily to determine the effect of the agent on the aggregation of dye in the dyebath.

Some Practical Aspects of the High-temperature Dyeing of Continuous-filament Yarns of Man-made Fibres

J. FOWLER and K. WALSH

The theoretical advantages of high-temperature dyeing are now generally recognised. Some of the practical aspects and the problems encountered are discussed on the basis of several years' experience in this specialised field.

During the last few years the high-temperature dyeing machine for the dyeing of continuous-filament yarns has proved a most useful piece of apparatus for the dyer. On the basis of experience of the use of high-temperature package-dyeing machinery, the writers propose to discuss some of the practical implications of, and also some of the snags which can arise in, the dyeing of viscose rayon, nylon, and Terylene continuous-filament yarns.

MACHINES

In most types of package-dyeing machinery the circulation of the liquor is obtained by means of a centrifugal pump. Under normal atmospheric pressure, i.e. with the "open" type of machine, as the temperature of the liquor reaches the boil, the flow falls to approximately half that which is obtained at the normal dyeing temperature of 95°c., owing to the formation of steam in the pump itself.

Thus a machine dyeing viscose rayon cakes at the normal maximum dyeing temperature will produce a flow of, say, 1¼ gal. of liquor per lb. of goods per minute, but as the temperature increases towards the boil this will decrease steadily, finally reaching a figure of about 0·7 gal. per lb. per minute.

To prevent this happening, the flow circuit can be made a closed one, but there will now be a tendency for occluded air and steam to collect in the head of the dyeing chamber; in other words, the machine will be virtually under pressure. The flow will now revert to normal, fundamentally, of course, because the boiling point of the liquor has been raised. In order to equalise the pressures in the dyeing chamber and the expansion tank, which otherwise would have the effect of depressing the level of the liquor below the top packages, a single pipe connection is made between the two sections.

It must be pointed out at this stage, however, that other modifications must be carried out besides those mentioned, in order to allow for the increased pressures.

Working under these conditions, when a temperature above 110°c. is reached it is noticeable that the flow again begins to fall; in other words, the dye liquor is approaching a new boiling point. In order to overcome this tendency, regardless of the temperature desired, compressed air is injected into the system, sufficient being added to ensure that the total pressure in the system is increased by at least 10 lb./sq.in. It has been recommended from time to time that this extra pressure, or *static pressure*, as it is sometimes called, can be added even when dyeing at temperatures well below 100°c. if so desired, but we have never found any real advantage in doing this.

Three points stand out very clearly —

Firstly, a modern high-temperature package-dyeing machine is quite complicated, and demands a high standard of skill and vigilance from the operatives. Incorrect handling of the machine can be a source of potential danger, both to the operative and to his working associates.

Secondly, as one would expect, the initial expense of such a machine is high, and in addition steam costs are higher than with normal machines. In order to justify this expenditure, all dyeing procedures and times must be strictly controlled and supervised by the foreman dyer, working in collaboration with the works chemist. Formulae must be accurately established, and full use made of the excellent laboratory sampling machines which are now available. In addition, the choice of dyes is not the least important factor, many of these undergoing both physical and chemical changes at the higher temperatures used.

Thirdly, errors due to the "human element" should be minimised by the installation of auxiliary equipment, such as a flow-meter, temperature- and time-cycle control, and automatic flow-change devices. Temperature and time recorders can also be added to give a complete picture of the dyeing operation.

As one would expect with this type of machine, the steam running costs, as already mentioned, are high. As a comparison, if we start with water at 60°c. and the capacity of the machine is 500 gal., the amount of steam required to heat this water to 100°c. is 348 lb. at 70 lb./sq.in.; if we raise the temperature to 127°c., the amount of steam then required will be 627 lb., an increase of 80%.

Certain savings can be made by lagging the machine, and using the flash steam produced when the pressure is released, by passing it through calorifiers to heat up process or boiler-feed water.

VISCOSE RAYON YARNS

Rayon yarns may be dyed either in the form of spinners' cakes on formers, in the perforated basket, or, in the case of folded yarns, in cheese form. One of the most beneficial uses of high-temperature dyeing is the application of the Class C type of direct dyes. It is well known that these dyes are generally difficult to apply because of levelling faults, and some of them, despite temperature control and extended dyeing times, have not been practical propositions.

Although a much greater degree of levelness ensues and the dyeing time is reduced at temperatures higher than 100°c., the final exhaustion is generally lower, so that in order to economise in the use of these dyes, the dyebath should be cooled at a predetermined rate, after levelling has been achieved.

For guidance, dyemakers have issued from time to time literature classifying the degree of decomposition of direct dyes at high temperatures, although it is the alkaline conditions which generally form the principal factor.

NYLON YARNS

Nylon yarns also can be dyed in either cheese form, mock cake, or hank in the perforated basket, and here, again, increased levelling is obtained in a shorter time. Claims have been made that by dyeing under these conditions the inherent uneven dyeing affinity of nylon is overcome when using the acid or metal-complex dyes, but these claims do not appear to be borne out by practical experience.

TERYLENE YARNS

It is probably with respect to Terylene yarn that the greatest boon has been given to the trade by the introduction of high-temperature dyeing. We consider that carrier dyeing at its present stage is a very poor alternative, as levelling throughout a package is difficult to achieve.

The yarn is usually twisted to a minimum of 5 t.p.in., and particularly in the case of cheeses, a setting temperature at least equivalent to the maximum dyeing temperature is necessary in order to avoid contraction, which would make proper penetration impossible. The main class of dyes used for dyeing Terylene, namely the disperse dyes, are, however, not all suitable, as a few of them are liable to some form of decomposition with a consequent loss in depth and/or change in hue occurring mostly under slightly alkaline conditions.

The problem of producing heavy dyeings with adequate rubbing fastness on low-twist yarn in package form is still acute, several reduction–clears being sometimes necessary to produce the desired result, but it must be pointed out that too many such treatments can produce degradation of the yarn. The type of dispersing agent used, the low exhaustion of the dyes in heavy depths, the density of the packages, for example, are all factors which can influence the desired result.

Many dye manufacturers are well aware of this trouble, and are carrying out research work to improve their products in this respect.

Dyes able to withstand the very high temperatures of heat setting are generally also more difficult to apply evenly, but with co-operation between the yarn dyer and the cloth finisher, a satisfactory compromise can usually be effected.

WILLIAM TATTON & CO. LTD.
    BUXTON ROAD
        LEEK
            STAFFORDSHIRE

Discussion

Mr. J. GREENWOOD: How do the authors dry their packages?

Mr. FOWLER: The packages are unloaded from the machine, hydroextracted, and dried in the conventional type of drying chamber, in which warm air is circulated by means of fans, and the temperature and the humidity are controlled.

Mr. H. W. PARTRIDGE: Does the lecturer prefer to dye continuous-filament nylon and Terylene yarns in cheese or in mock-cake form?

Mr. WALSH: Taking into account several other factors, we find that both nylon and Terylene continuous-filament yarns are preferably dyed in cheese form at high temperature.

Mr. H. A. TURNER: In many places there is a reference to the need to adjust the top plate on the spindle as the packages settle down during the dyeing. Would it not be possible to do this automatically by a suitable arrangement of compression springs bearing downward on this plate?

Mr. FOWLER: At the present time, various methods are being tried to overcome the necessity of having to depress the top plate on the spindle at intervals during the dyeing process to maintain good package-to-package contact. As yet, none has been found which is entirely satisfactory.

Mr. L. HUGHES: Would not an improvement in the penetration of the fibre and a corresponding increase in exhaustion of many dyes result from working at static pressures of about 40 lb./sq.in. at temperatures below the boil as well as above?

Mr. FOWLER: In our experience, no advantage is to be gained by increasing the applied pressure above 10 lb./sq.in. at temperatures either above or below the boil. We find no justification for assuming that any significant increase in either diffusion or exhaustion will take place with these increased pressures.

Mr. H. R. HADFIELD*: Would the authors confirm that, in their experience, good flow at temperatures approaching the boil is obtained in normal, closed, package-dyeing machines if a static pressure is built up by sealing the air in the machine? This improved flow, by avoidance of cavitation, is obtained, unfortunately, only in machines in perfect mechanical condition. Any leakage will gradually allow the static pressure to fall, and, in the absence of a topping-up pressure, cavitation will result.

Mr. FOWLER*: We do confirm the points brought out in this question.

* Communicated.

The Dyeing of Nylon with Acid and Mordant Dyes at High Temperatures

H. R. HADFIELD and H. SEAMAN

A study has been made of the stability of acid and chrome dyes in solution at temperatures above 100°C. The effects of an increase in dyeing temperature above 100°C. on the levelling of acid dyes and upon the rate of chroming of chrome dyes have also been determined. The results emphasise the importance of controlling the exhaustion of the dyebath during the dyeing of nylon and confirm the rapid rate of chroming above 100°C.

Introduction

Studies of the effect of temperatures above 100°C. on the application of acid dyes to wool [1-3] have shown a large improvement in level dyeing. Although it has been generally assumed that a similar improvement is obtained on nylon, no quantitative results have been available. The detailed work described here was designed to obtain these results and also to determine the effect of high-temperature dyeing upon the covering of nylon yarns of different dyeing properties.

Experimental

1. MATERIALS

(a) TEXTILES— (i) Micro-dull continuous-filament nylon yarn of 45 denier and 15 filaments, with a saturation value of 1·02 g. of Naphthalene Scarlet 4RS (C.I. Acid Red 18) per 100 g. of nylon [4].

(ii) Continuous-filament nylon fabric containing warp threads with known differences in orientation and amine end-group content.

(iii) Continuous-filament nylon twill fabric.

(b) CHEMICALS— Commercially available quality.

2. DYEING APPARATUS

Dyeings and levelling tests at 95°C. were carried out in a Marney dyeing machine; for those at higher temperatures the small-scale rotating machine described by Graham and Jamin [5] was used.

3. SCOURING

All yarns and fabrics were scoured, before dyeing, in a liquor containing 2 parts of Lissapol N and 1 part of soda ash per 1,000 parts, at 70°C. for 20 min., and then thoroughly rinsed in cold water.

4. INVESTIGATION OF THE STABILITY OF ACID DYES

A standard depth of each dye was applied to nylon yarn, at 95°C. and at 130°C. for 1 hr., from a bath containing sufficient acetic acid or formic acid to produce the maximum exhaustion. The liquor ratio employed was 40:1. The dyeings were then rinsed in cold water and dried. The colours of the dyeings at 95°C. and 130°C. were compared visually.

5. MEASUREMENT OF THE LEVELLING OF ACID DYES

The measurements of levelling were carried out as follows— The dyebath was set with the dissolved dye and all the dyeing assistants, the liquor ratio being 40:1 in every case. Two hanks of nylon yarn, each weighing 1 g., were placed in the bath, and dyeing was carried out for 45 min. The exhaustion of the dyebath was then measured by comparing the optical density of the dye liquor with that of a solution containing a known quantity of dye and quantities of dyebath assistants corresponding to those in the dye liquor.

One hank was removed from the dyebath and replaced by an equal weight of undyed nylon.

Levelling was then allowed to take place, at the dyeing temperature, for 45 min. Both the dyed and the levelled hanks were then removed from the bath, rinsed in cold water, and dried. The amounts of dye taken up by each of these hanks were then determined by dissolving 0·5 g. of the nylon in 100 ml. of formic acid (85%), and measuring the optical density of the solution. This value was then compared with the optical density of a known quantity of the dye and 0·5 g. of undyed nylon in 100 ml. of formic acid (85%). All optical-density measurements were made with a Hilger Spekker absorptiometer.

The measurements of levelling were carried out at 95°, 110°, and 130°c. for each dye used. The conditions of exhaustion were varied, at each of these temperatures, by adjustment of the pH. The dyebath was prepared with 6·8 g. of potassium dihydrogen phosphate per litre, and sufficient 0·2 N. caustic soda solution or 0·2 N. hydrochloric acid to produce the required pH.

6. INVESTIGATION OF THE EFFECT OF HIGH DYEING TEMPERATURE ON THE COVERING OF YARN IRREGULARITIES

The nylon fabric containing warp threads having known differences in orientation and amine end-group content was dyed with a number of acid dyes, for 45 min., at 95°c. and at 130°c. The liquor ratio was 40:1. A dyebath exhaustion of approx. 80% was achieved by preparing the bath with 6·8 g. of potassium dihydrogen phosphate per litre, and adding 0·2 N. caustic soda solution or 0·2 N. hydrochloric acid until the desired conditions were obtained. The nylon fabric was then rinsed in cold water and dried.

The amount of dye taken up by the warp threads was then estimated by withdrawing these threads from the fabric, dissolving them in formic acid (85%), and comparing the optical densities of the solutions with that of a solution of a known quantity of dye and nylon in formic acid (85%). These optical-density measurements were all made with a Hilger Spekker absorptiometer.

7. INVESTIGATION OF THE STABILITY OF CHROME DYES

(a) Each dye was dissolved in distilled water, and 60-ml. portions of the solution were heated at 100°, 120°, and 130°c. for 1 hr. The heated solutions and a portion of the unheated solution were diluted and buffered with ammonia or acetic acid, and measurements of optical density were then made over the wavelength range 380–700 mμ. with a G.E.C. recording spectrophotometer, and in some cases over the range 352–380 mμ. with a Unicam SP 600 spectrophotometer.

(b) Each dye was applied to nylon twill fabric at 95°c. and 130°c. for 1 hr. from baths containing 4% formic acid (85%). The dyeing at 130°c. was chromed at 130°c. for 20 min. in a bath containing potassium dichromate and 4% formic acid (85%). The dyeing at 95°c. was chromed at 95°c. in a bath containing potassium dichromate and 4% formic acid (85%) for 1 hr., sodium thiosulphate (double the quantity of dichromate used) was then added

to the bath, and chroming was continued for 30 min. The quantities of potassium dichromate used were—

0–2% Dye 0·5% Potassium dichromate
2–6% Dye 1·0% Potassium dichromate
>6% Dye 2·0% Potassium dichromate

The colour and washing fastness of the dyeings at 95°c. and 130°c. were compared.

8. INVESTIGATION OF THE EFFECT OF HIGH TEMPERATURES UPON CHROMING

Standard depths of Solochrome Yellow C (C.I. Mordant Yellow 16), Solochrome Brown RH (C.I. Mordant Brown 33), and Solochrome Azurine B (C.I. Mordant Blue 1) were applied to nylon yarn at 95°c. for 1 hr. in baths containing 4% formic acid (85%). Each dye was then chromed at 130°c. using 4% formic acid (85%) and 0·5%, 1·0%, and 2·0% potassium dichromate. The times of chroming were 5, 10, 15, 30, and 45 min. The colours obtained were compared.

Results and Discussion

1. STABILITY OF ACID DYES

Although the stability of acid dyes used for dyeing wool above 100°c. has been studied [3], these results are not necessarily of value for the dyeing of nylon. The reasons for any differences are the possible protective effect of dye already absorbed on fibres, the different degree of absorption of the same dye applied to wool and to nylon, and the chemical reactivity of the individual fibres. Dyeings were therefore carried out at 95°c. and at 130°c. for 1 hr. and then compared for colour. In both cases the exhaustion of the dye on to the fibre was approx. 100%, and this eliminated the possibility of exhaustion effects obscuring the results. The stable dyes are listed in Table I, and the unstable

TABLE I

Acid Dyes suitable for Dyeing at High Temperatures

Dye	Colour Index No.
A— LEVEL-DYEING ACID DYES	
Lissamine Flavine FF	C.I. Acid Yellow 7
Quinoline Yellow A	C.I. Acid Yellow 3
Propolan Yellow 3G	C.I. Acid Yellow 29
Lissamine Fast Yellow 2G	C.I. Acid Yellow 17
Tartrazine N	C.I. Acid Yellow 23
Azo Yellow FFN	C.I. Acid Yellow 6
Citronine R	C.I. Acid Orange 1
Metanil Yellow YK	C.I. Acid Yellow 36
Lissamine Fast Yellow AE	C.I. Acid Orange 3
Naphthalene Fast Orange 2G	C.I. Acid Orange 10
Naphthalene Orange G	C.I. Acid Orange 7
Naphthalene Orange RO	C.I. Acid Orange 8
Naphthalene Scarlet R	C.I. Acid Red 26
Croceine Scarlet 3B	C.I. Acid Red 73
Naphthalene Scarlet B	C.I. Acid Red 102
Naphthalene Scarlet 4R	C.I. Acid Red 18
Naphthalene Red J	C.I. Acid Red 88
Naphthalene Red EA	C.I. Acid Red 13
Lissamine Fast Red 3G	C.I. Acid Red 5
Lissamine Fast Red B	C.I. Acid Red 37
Azo Geranine 2G	C.I. Acid Red 1
Carmoisine W	C.I. Acid Red 14
Carmoisine L	C.I. Acid Red 12

TABLE I— *continued*

Dye	*Colour Index* No.
Naphthalene Bordeaux B	C.I. Acid Red 17
Lissamine Rhodamine B	C.I. Acid Red 52
Propolan Red 3G	C.I. Acid Red 57
Solway Rubinol R	C.I. Acid Red 80
Lissamine Red 6B	C.I. Acid Violet 7
Lissamine Red 7BP	C.I. Acid Violet 5
Lissamine Violet 2R	C.I. Acid Violet 1
Solway Purple R	C.I. Acid Violet 43
Lissamine Violet 10B	C.I. Acid Blue 13
Solway Blue RN	C.I. Acid Blue 47
Lissamine Ultra Sky R	C.I. Acid Blue 67
Solway Ultra Blue B	C.I. Acid Blue 25
Lissamine Ultra Blue AR	C.I. Acid Blue 71
Solway Blue BN	C.I. Acid Blue 45
Solway Blue A	C.I. Acid Blue 69
Solway Blue G	C.I. Acid Blue 37
Solway Blue 2G	C.I. Acid Blue 40
Solway Celestol B	C.I. Acid Blue 27
Disulphine Blue FFN	C.I. Acid Blue 147
Disulphine Blue VN	C.I. Acid Blue 1
Disulphine Blue AN	C.I. Acid Blue 7
Lissamine Green BN	C.I. Acid Green 50
Naphthalene Dark Green A	C.I. Acid Green 20

B— ACID MILLING DYES

Dye	*Colour Index* No.
Coomassie Yellow 7G	C.I. Acid Yellow 44
Coomassie Yellow 6G	C.I. Direct Yellow 8
Carbolan Yellow 4G	C.I. Acid Yellow 70
Carbolan Yellow 3G	C.I. Acid Yellow 72
Carbolan Yellow R	C.I. Acid Yellow 71
Coomassie Yellow R	C.I. Acid Yellow 42
Coomassie Fast Orange G	C.I. Acid Orange 33
Carbolan Fawn R	C.I. Acid Brown 49

TABLE I— *continued*

Dye	*Colour Index* No.
Coomassie Brown G	C.I. Acid Brown 22
Coomassie Fast Brown R	C.I. Acid Orange 51
Coomassie Fast Scarlet 2G	C.I. Acid Red 140
Coomassie Milling Scarlet G	C.I. Acid Red 97
Coomassie Fast Scarlet B	C.I. Acid Red 111
Coomassie Red PG	C.I. Acid Red 85
Coomassie Milling Scarlet 5B	C.I. Acid Red 89
Coomassie Red BR	C.I. Acid Red 158
Coomassie Red G	C.I. Acid Red 116
Coomassie Geranine 2G	—
Carbolan Crimson B	C.I. Acid Red 138
Carbolan Crimson 3B	C.I. Acid Red 139
Coomassie Violet 2R	C.I. Acid Violet 9
Solway Violet BR	C.I. Acid Violet 34
Solway Violet BN	C.I. Acid Violet 34
Coomassie Bordeaux B	—
Carbolan Violet 2R	C.I. Acid Violet 51
Coomassie Blue BL	C.I. Acid Blue 59
Coomassie Blue GL	C.I. Acid Blue 102
Carbolan Brilliant Blue 2R	C.I. Acid Blue 140
Coomassie Brilliant Blue R	C.I. Acid Blue 83
Solway Sky Blue B	C.I. Acid Blue 78
Carbolan Blue B	C.I. Acid Blue 138
Coomassie Navy Blue D	C.I. Acid Black 26A
Coomassie Navy Blue 2RN	C.I. Acid Blue 113
Coomassie Navy Blue GN	C.I. Acid Blue 120
Coomassie Fast Green GN	C.I. Acid Green 25
Carbolan Brilliant Green 5G	C.I. Acid Green 28
Solway Green G	C.I. Acid Green 25
Carbolan Green G	C.I. Acid Green 27
Coomassie Fast Grey 3G	C.I. Acid Black 48
Coomassie Fast Black B	C.I. Acid Black 24
Coomassie Fast Black G	C.I. Acid Black 21

TABLE II
Acid Dyes unsuitable for Dyeing at High Temperatures

Dye	*Colour Index* No.	Change in Colour
A— LEVEL-DYEING ACID DYES		
Tartrazine K	C.I. Acid Yellow 27	3 duller
Citronine Y	C.I. Acid Yellow 63	2 duller
Naphthalene Brown R	C.I. Acid Brown 6	2 redder, duller
Lissamine Fast Red 4G	C.I. Acid Red 30	2 yellower, brighter
Lissamine Rhodamine G	C.I. Acid Red 50	3 bluer
Acid Magenta A	C.I. Acid Violet 19	1
Naphthalene Purple A	C.I. Acid Violet 62	2 bluer
Lissamine Fast Violet 2B	C.I. Acid Violet 41	3 redder, duller
Lissamine Violet 6BN	C.I. Acid Violet 15	1
Lissamine Blue BF	C.I. Acid Blue 18	3–4 redder
Indigo Carmine X	C.I. Acid Blue 74	1
Lissamine Navy Blue 3G	C.I. Acid Blue 6	2 weaker, greener
Disulphine Green B	C.I. Acid Green 9	1
Naphthalene Green G	C.I. Acid Green 3	1
Lissamine Green SF	C.I. Acid Green 5	1
Lissamine Green V	C.I. Acid Green 16	1
Naphthalene Black 12B	C.I. Acid Black 1	4 redder
Naphthalene Blue Black C	C.I. Acid Black 41	3 greener
B— ACID MILLING DYES		
Coomassie Fast Yellow G	C.I. Acid Yellow 85	2 redder
Coomassie Red R	C.I. Acid Red 99	3
Coomassie Violet R	C.I. Acid Violet 17	1 redder
Coomassie Blue RL	C.I. Acid Blue 92	3 redder
Coomassie Brilliant Blue FF	C.I. Acid Blue 15	2
Coomassie Ultra Sky SE	C.I. Acid Blue 112	1 stronger, redder
Coomassie Brilliant Blue G	C.I. Acid Blue 90	2 redder
Coomassie Navy Blue G	C.I. Acid Blue 118	2 weaker, greener
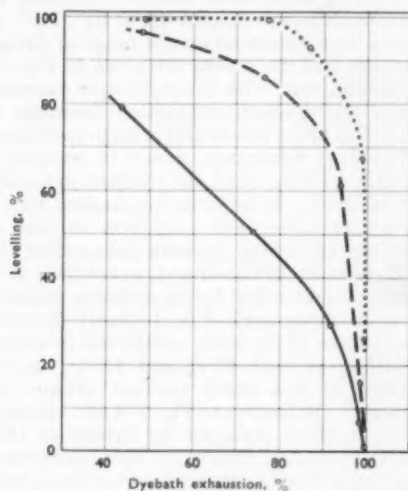
FIG. 1— 1·0% Carbolan Blue BS (C.I. Acid Blue 138)
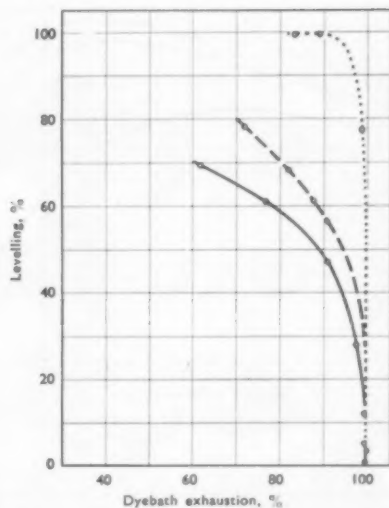
FIG. 2— 1·0% Coomassie Red PGS (C.I. Acid Red 85)
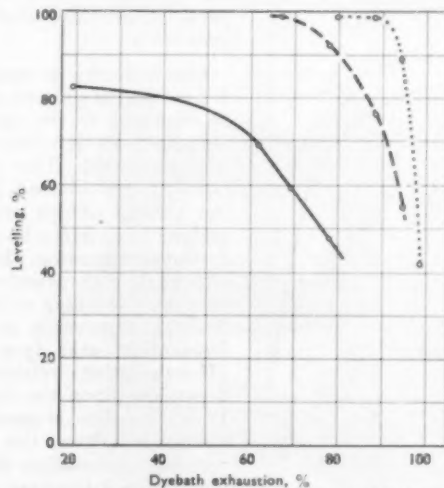
FIG. 3— 0·5% Naphthalene Scarlet 4RS (C.I. Acid Red 18)

```
--- O ---   130°C.
-- O --     110°C.
—— O ——     95°C.
```

FIG. 1–3— Effect of Dyebath Exhaustion on Levelling

dyes are listed in Table II, together with a description of the change of colour observed. Clearly, unstable dyes are to be avoided wherever possible, as, in addition to what is generally an undesirable change in colour, there may be also a deterioration in an important fastness property and a lack of reproducibility. The vast majority of acid dyes examined are, however, stable at elevated temperatures, and no difficulty should be experienced from any serious diminution in the range of dyes available.

2. LEVELLING BEHAVIOUR OF ACID DYES

It is known that on wool and on nylon the levelling of acid dyes depends upon the exhaustion as well as upon the temperature of the dyebath [6, 7]. It was therefore decided that, in the study of the effect of elevated temperatures upon the levelling of acid dyes, the influence of dyebath exhaustion should also be determined. The exhaustion of acid dyes on nylon can be controlled by varying the pH of the dyebath or by using a complex anionic competing agent. In the present series of tests, control of dyebath pH was employed in order to avoid complicating effects. The degree of levelling was expressed quantitatively as—

$$\text{Levelling (\%)} = \frac{\text{Dye on the levelled nylon}}{\text{Dye on the initially dyed nylon}} \times 100$$
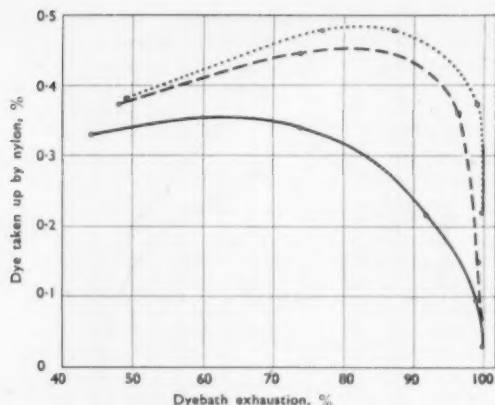
FIG. 5— 1·0% Carbolan Blue BS (C.I. Acid Blue 138)
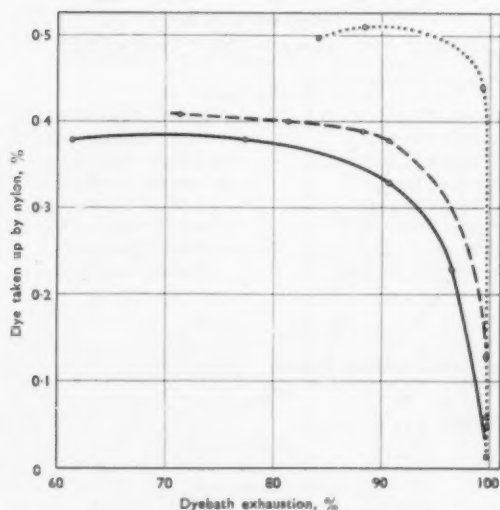
FIG. 6— 1·0% Coomassie Red PGS (C.I. Acid Red 85)
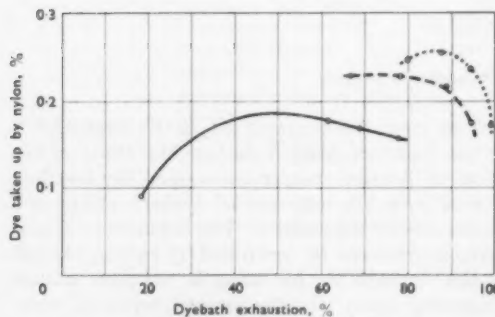
FIG. 7— 0·5% Naphthalene Scarlet 4RS (C.I. Acid Red 18)

```
--- O --- 130°C.
—— O —— 110°C.
——O—— 95°C.
```

FIG. 5-7— Effect of Exhaustion on Dye taken up by Undyed Nylon

The levelling of Carbolan Blue B, Coomassie Red PG, and Naphthalene Scarlet 4R at 95°, 110°, and 130°c. has been measured over a range of dyebath exhaustions, and the results are given in Fig. 1–3. It will be seen that, with the three dyes examined, increasing the dyebath exhaustion decreases the levelling. This effect is sufficiently large to eliminate in practice any advantage gained in levelling by dyeing above 100°c. when the dyebath exhaustion is close to 100%. It must be emphasised that, in the dyeing of nylon with acid dyes to pale and medium depths, a high dyebath exhaustion, close to 100%, is easily obtained and, in contrast to the behaviour of most other dyeing systems, cannot be regarded as uncommon. Fig. 4 clearly illustrates the importance of dyebath exhaustion in controlling levelling at both 95°c. and 130°c., but the significance of this effect has not always been appreciated[1]. Reference to Fig. 1–4 also shows the improved levelling obtained by dyeing at 110°c. and 130°c. compared with 95°c. This improvement is very marked with dyebath exhaustions below 95%, and they clearly illustrate the advantageous effect upon levelling of an elevated dyeing temperature, provided that the dyebath exhaustion is controlled.

One difficulty in interpreting the results in Fig. 1–3 is that they do not readily allow information to be obtained on the optimum dyebath conditions for maximum levelling consistent with maximum tinctorial yield. This important information can, however, be obtained from Fig. 5–7, which show the amount of dye migrating on to the initially undyed hank in the levelling test in relation to the dyebath exhaustion. From these results it will be seen that, with practically all the dyes examined, maximum levelling at 95–130°c. is obtained with a dyebath exhaustion in the range 80–90%. Unfortunately, acid dyes are not uniform in their pH–exhaustion relation, which is also very dependent upon the depth of colour being dyed. It is therefore suggested that, before practical dyeing is begun, the dyebath pH to give the optimum exhaustion should be determined by a qualitative laboratory test. Suitable buffers for use in nylon dyebaths, giving a wide pH range, have been detailed by dyemakers[6].

3. IRREGULARLY DYEING YARNS

Munden and Palmer[4, 5] have determined the cause of irregularly dyeing nylon yarns. These workers have shown that chemical differences, resulting mainly from differences in amino groups in the yarn, cause differences in acid dye absorption which are maintained at equilibrium; but the dyeing irregularities resulting from physical variations in the yarn are often covered if dyeing is allowed to continue to equilibrium, as physical variations affect mainly the rate of dye absorption. In practical dyeing with acid dyes, however, the dyeing is rarely allowed to proceed to equilibrium, and at the end of the dyeing period the dye distribution between yarns having different physical characteristics reflects the differences in the initial rates of dye absorption. If, however, levelling

Coomassie Red PG (C.I. Acid Red 85)

Temperature	Dyebath Exhaustion
95°C.	100%
130°C.	100%
95°C.	80%
130°C.	80%
95°C.	100%
130°C.	100%
95°C.	80%
130°C.	80%
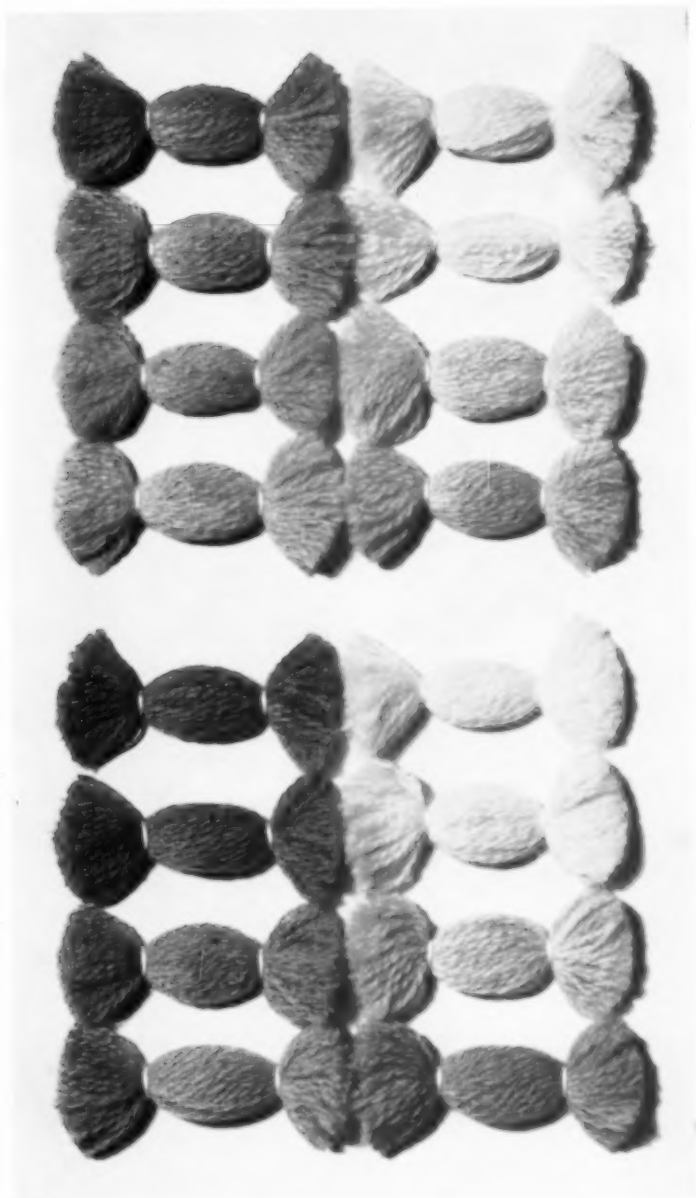
Carbolan Blue B (C.I. Acid Blue 138)

Fig. 4— The Levelling of Acid Dyes on Nylon
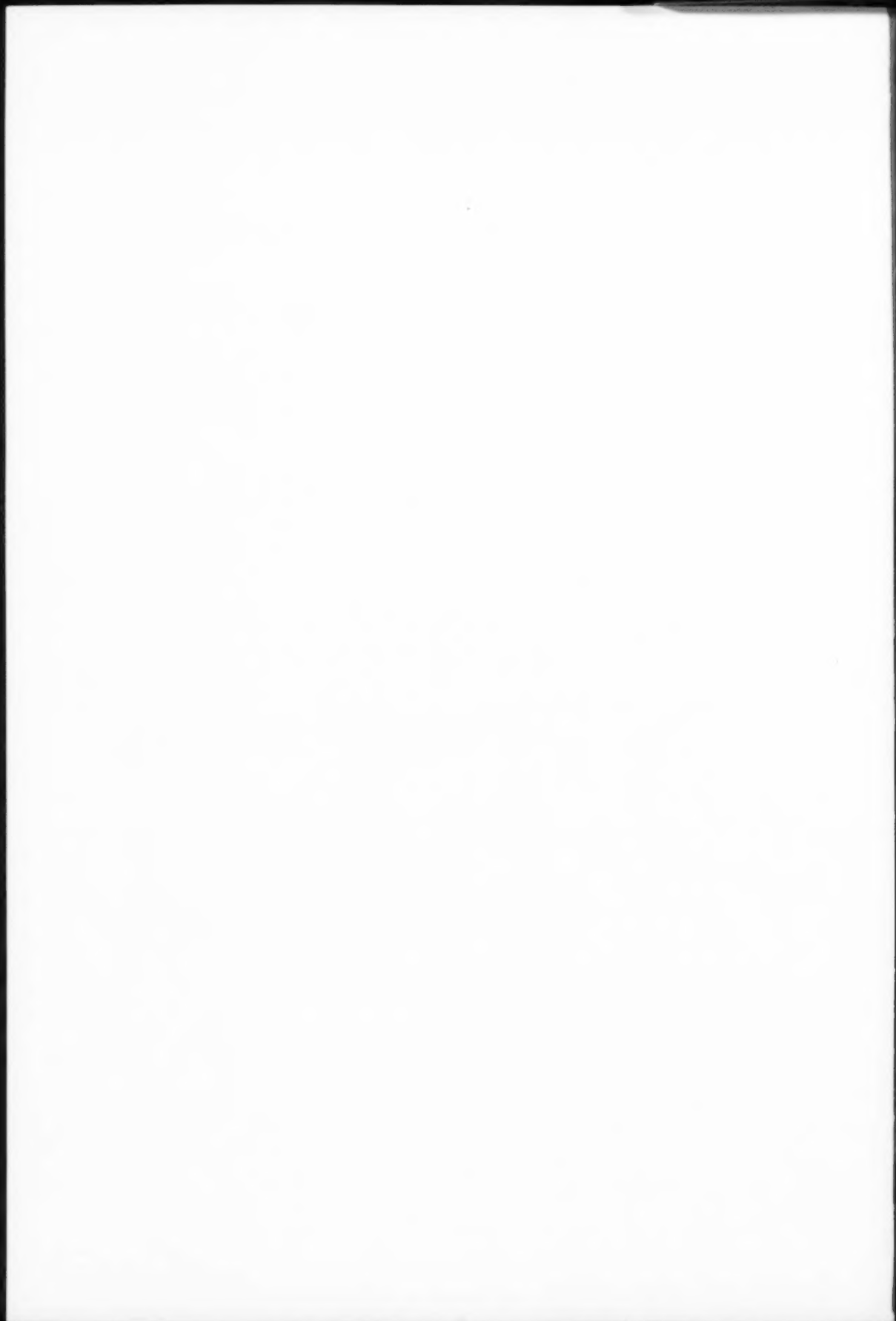
TABLE III
Coverage of Irregular Yarns

| Dye | Colour Index No. | | Nylon | | Dye on Fibre | |
| | | | Orientation | Amine End-group Content | Dye on Nylon A | |
					95°c.	130°c.
1·0% Coomassie Fast Orange GS	C.I. Acid Orange 23	B	Abnormal	Normal	1·26	1·13
		A	Normal	Normal	1	1
		C	Normal	Abnormal	0·76	0·87
1·5% Coomassie Red PGS	C.I. Acid Red 85	B	Abnormal	Normal	1·11	1·07
		A	Normal	Normal	1	1
		C	Normal	Abnormal	0·72	0·72
1·0% Naphthalene Scarlet 4RS	C.I. Acid Red 18	B	Abnormal	Normal	1·20	1·06
		A	Normal	Normal	1	1
		C	Normal	Abnormal	0·77	0·76
2·0% Carbolan Blue BS	C.I. Acid Blue 138	B	Abnormal	Normal	1·26	0·985
		A	Normal	Normal	1	1
		C	Normal	Abnormal	0·86	0·75
1·5% Coomassie Navy Blue 2RNS	C.I. Acid Blue 113	B	Abnormal	Normal	1·12	1·05
		A	Normal	Normal	1	1
		C	Normal	Abnormal	0·85	0·83

could be facilitated, then redistribution of dye could proceed after the initial absorption, and improvement in the coverage of physical irregularities in the yarns could be expected. With a suitable dyebath pH to give an exhaustion of approx. 80%, in order to encourage levelling, the effect of raising the dyeing temperature from 95° to 130°c. on the covering of irregularly dyeing yarns has been determined (Table III). In every case examined a significant improvement in the coverage of physical irregularities in the yarns results from dyeing at 130°c. instead of at 95°c. This confirms the results of Brooks and Reith [9]. These workers, however, adjusted the exhaustion of the dyebath by using a complex anionic agent to compete with the dye for the fibre.

TABLE IV
Decomposition of Chrome Dyes in Solution

| Dye | Colour Index No. | Decomposition (%) in 1 hr. | | |
		100°c.	120°c.	130°c.
Solochrome Flavine G	C.I. Mordant Yellow 5	1	3	3
Solochrome Yellow C	C.I. Mordant Yellow 16	4	5	9
Solochromate Fast Yellow R	—	1	2	4
Solochrome Flavine R	C.I. Mordant Yellow 8	2	2	3
Solochrome Orange M	C.I. Mordant Orange 1	4	4	7
Solochrome Orange GR	C.I. Mordant Orange 6	—	—	6
Solochromate Fast Orange 2R	C.I. Mordant Orange 12	0	9	28
Solochrome Yellow 2GN	C.I. Mordant Yellow 12	0	0	0
Solochromate Fast Brown 3G	C.I. Mordant Brown 24	0	0	6
Solochromate Fast Brown G	—	5	5	9
Solochrome Brown EB	C.I. Mordant Brown 1	13	13	15
Solochrome Brown RH	C.I. Mordant Brown 33	2	3	7
Solochrome Brown P	C.I. Mordant Brown 31	6	12	13
Solochrome Brown RG	C.I. Mordant Brown 29	2	3	5
Solochromate Fast Red 6G	C.I. Mordant Red 1	3	10	19
Solochrome Red D	C.I. Mordant Red 14	—	3	4
Solochrome Red ER	C.I. Mordant Red 7	40	63	68
Solochromate Fast Bordeaux BN	—	6	9	16
Solochrome Violet R	C.I. Mordant Violet 5	7	9	10
Solochrome Brilliant Violet R	C.I. Mordant Violet 1	—	3	24
Solochrome Brilliant Violet BR	C.I. Mordant Violet 8	10	14	17
Solochrome Azurine B	C.I. Mordant Blue 1	2	—	68
Solochromate Fast Blue B	C.I. Mordant Blue 7	37	61	75
Solochrome Dark Blue B	C.I. Mordant Black 17	14	44	59
Solochromate Fast Olive B	C.I. Mordant Green 26	8	13	24
Solochromate Fast Grey B	C.I. Mordant Black 38	23	63	81
Solway Blue Black B	C.I. Mordant Black 13	11	29	44
Solochrome Black 6BN	C.I. Mordant Black 3	55	83	89
Solochrome Black F	C.I. Mordant Black 5	7	9	20
Solochrome Black PV	C.I. Mordant Black 9	13	34	51
Solochrome Black PG	C.I. Mordant Black 7	1	13	24
Solochrome Black WDFA	C.I. Mordant Black 11	49	77	87

4. STABILITY OF CHROME DYES

The majority of chrome dyes are similar to acid dyes in dyeing properties, and it is therefore reasonable to assume that the same advantages are to be gained by high-temperature dyeing, in so far as levelling behaviour is concerned. The stability of chrome dyes in dye liquors at 100°c. and above was determined by comparing the spectral absorption curves of the dyes after solutions in distilled water had been heated for 1 hr. at 100°, 120°, and 130°c. with those obtained from unheated solutions of the dyes. The results obtained are detailed in Table IV. The interpretation of these results should be made with care, as it is very probable that the dye absorbed on the fibre is protected, in some degree, from decomposition. The results should be used as an indication of the relative stability of chrome dyes and also as an indication of the maximum amount of dye that may be decomposed during dyeing.

In order to obtain a more practical assessment of the stability of chrome dyes in actual dyeing processes, an alternative method of assessing stability was also used. Dyeings were carried out on nylon at 95° and 130°c. for 1 hr. from an acidic dyebath. Subsequently, both dyeings were chromed, those dyes applied at 130°c. being chromed at 130°c. for 20 min., and those applied at 95°c. being chromed at 95°c. for 90 min. A comparison was then made of the colour and washing fastness of the two sets of dyeings. It was found possible to divide the dyes into three classes—

(1) Suitable for application to nylon at both 95° and 130°c.

(2) Suitable for application at 95°, but not at 130°c. because of decomposition

(3) Suitable for application at 130°c., but not at 95°c. because of incomplete chroming.

The classification of selected chrome dyes in the above three classes is detailed in Table V.

It must be understood, however, that in this evaluation the two extreme temperatures of application were selected. It is possible that certain chrome dyes which have been found unsuitable for application at 130°c. because of decomposition, either at the dyeing or at the chroming stage, may show advantages in dyeing at e.g. 110° compared with 95°c. In most cases dyeing and chroming at 110° will show advantages over 95°c., and dye instability will not be troublesome. The method of dyeing also will affect the stability of the dye. In the tests described, a standard technique—dyeing from a dyebath containing 4% formic acid (85%)—was adopted. In practical dyeing it may be desirable to obtain a lower rate of dyeing by suitable adjustment of the dyebath pH. This latter technique results in the presence in the dyebath for a longer period of unabsorbed dye, with a consequent greater possibility of dye decomposition.

5. EFFECT OF HIGH TEMPERATURES UPON CHROMING

Solochrome Yellow C, Solochrome Brown RH, and Solochrome Azurine B were applied to nylon at 95°c. and then chromed at 130°c. for 5, 10, 15,

TABLE V

Preferred Temperatures of Application for Chrome Dyes

Dye	Colour Index No.
A— DYES SUITABLE FOR APPLICATION AT 95°c. AND 130°c.	
Solochrome Flavine G	C.I. Mordant Yellow 5
Solochrome Yellow 3G	C.I. Mordant Yellow 18
Solochrome Yellow 2G	C.I. Mordant Yellow 10
Solochrome Yellow C	C.I. Mordant Yellow 16
Solochromate Fast Yellow R	—
Solochrome Flavine R	C.I. Mordant Yellow 8
Solochrome Orange M	C.I. Mordant Orange 1
Solochrome Orange GR	C.I. Mordant Orange 6
Solochromate Fast Orange 2R	C.I. Mordant Orange 12
Solochrome Yellow 2GN	C.I. Mordant Yellow 12
Solochromate Fast Brown 3G	C.I. Mordant Brown 24
Solochrome Brown EB	C.I. Mordant Brown 1
Solochrome Brown RH	C.I. Mordant Brown 33
Solochrome Brown P	C.I. Mordant Brown 31
Solochrome Brown RG	C.I. Mordant Brown 29
Solochrome Red D	C.I. Mordant Red 14
Solochrome Violet R	C.I. Mordant Violet 5
*Solochrome Brilliant Violet BR	C.I. Mordant Violet 8
Solochromate Fast Olive B	C.I. Mordant Green 26
*Solway Blue Black B	C.I. Mordant Black 13
*Solochrome Black 6BN	C.I. Mordant Black 3
Solochrome Black F	C.I. Mordant Black 5
Solochrome Black WDFA	C.I. Mordant Black 11
B— DYES SUITABLE FOR APPLICATION AT 95°c. BUT NOT AT 130°c.	
Solochromate Fast Brown G	—
Solochromate Fast Red 6G	C.I. Mordant Red 1
Solochrome Red ER	C.I. Mordant Red 7
Solochromate Fast Bordeaux BN	—
Solochrome Brilliant Violet R	C.I. Mordant Violet 1
Solochrome Azurine B	C.I. Mordant Blue 1
Solochromate Fast Blue B	C.I. Mordant Blue 7
Solochrome Dark Blue B	C.I. Mordant Black 17
Solochromate Fast Grey B	C.I. Mordant Black 38
C— DYES SUITABLE FOR APPLICATION AT 130°c. BUT NOT AT 95°c.	
Solochrome Black PV	C.I. Mordant Black 9
Solochrome Black PG	C.I. Mordant Black 7

* Superior results obtained at 130°c.

30, and 45 min. using 0·5, 1·0, and 2·0% of potassium dichromate. The results showed that, in all three cases, full chromation was achieved in 10 min. with 0·5% of potassium dichromate. If the above three dyes are chromed at 95°c. to obtain the same result, it is necessary to chrome for 1 hr. It is therefore clear that high-temperature dyeing offers very real advantages for applying this class of dye. In the case of heavy depths, such as blacks and very heavy navy blues and dark browns, the chroming time at 130°c. should be extended to 15–20 min. and the quantity of mordant increased from 0·5 to 2·0% in order to ensure complete metallisation. There is no need to add reducing agents to complete the development of the colour[10] when high-temperature chroming is employed.

Attempts have been made to use alternative chroming agents to potassium dichromate. Salts, such as chromium sulphate, chloride, and acetate, have been evaluated and found to be of no value,

as no chromation results unless the quantity of the chromium salt is increased to approx. 30%.

DYEHOUSE DEPARTMENT
IMPERIAL CHEMICAL INDUSTRIES LTD.
DYESTUFFS DIVISION
HEXAGON HOUSE
MANCHESTER 9

(*MS. received 12th June 1957*)

References

[1] AATCC Philadelphia Section, *Amer. Dyestuff Rep.*, 38, P 9 (1949).

[2] Drijvers, *ibid.*, 41, 533 (1952).

[3] Coutie, Lemin, and Sagar, J.S.D.C., 71, 433 (1955).

[4] Palmer, *ibid.*, 67, 609 (1951).

[5] Graham and Jamin, *Hexagon Digest*, No. 24, 19 (Oct. 1956).

[6] ICI, *Technical Information*, Dyehouse No. 207 (1954).

[7] Lemin and Rattee, J.S.D.C., 65, 217 (1949).

[8] Munden and Palmer, *J. Textile Inst.*, 41, P 609 (1950).

[9] Brooks and Reith, *Amer. Dyestuff Rep.*, 44, 698 (1955).

[10] Hadfield and Sharing, J.S.D.C., 64, 381 (1948).

[11] Peters, H. W., and Turner, J. C., *ibid.*, 74, 252 (April 1958).

[12] Fowler, J., and Walsh, K., *ibid.*, 74, 390 (May 1958).

Discussion

Mr. J. GREENWOOD: The authors do not publish exhaustion rates of chrome dyes. Do they get complete exhaustion? If so, this would materially reduce the processing time.

Mr. HADFIELD: In our work on the application of chrome dyes to nylon above 100°c. we have observed that, generally, superior exhaustion of the chrome dye into the nylon is obtained. Complete exhaustion is not achieved, however, and for this reason chroming in the same dyebath cannot be recommended. The improvement in time of processing achieved by applying chrome dyes above 100°c. results purely from a reduction in the dyeing time and a reduction in the chroming time.

Miss ESMÉE SMITH: Have you noticed any appreciable increase in uptake of chrome dye when heavy depths are applied to nylon at high temperatures?

Mr. HADFIELD: In a large number of cases we have obtained superior tinctorial yield by dyeing at 130°c. instead of 100°c.

Mr. C. HOBDAY: In view of observations made by previous lecturers [11, 12], that the high-temperature dyeing of irregular nylon gives little improvement in the coverage of physical variations, it is interesting to note that the lecturers have obtained a significant improvement in this direction by dyeing at 130°c. I should like to know whether trials under bulk conditions have confirmed their laboratory investigations, and if so, whether the result obtained gives a fabric which is commercially acceptable?

Mr. HADFIELD: The particular point of this question is discussed at length in the paper presented. We therefore emphasise that, with dyeing conditions under which the exhaustion of the dyebath is high, then, no matter what temperature of dyeing is achieved, no levelling of dye is found. Under these conditions, covering of yarn irregularities at both 95°c. and 130°c. is low, and no significant difference between the two temperatures can be found. If, however, the dyebath conditions are adjusted so that the dye is not completely exhausted, the exhaustion approximating to 80%, then by raising the dyeing temperature of 95°c. to 130°c. an appreciable improvement is obtained in coverage of irregularities in the nylon resulting from physical differences. As described in the paper, no improvement is obtained in coverage of irregularities in the nylon yarn resulting from chemical differences.

We agree that these results appear to contradict the work referred to [11, 12], and we can only assume that in this case the dyebath conditions were not adjusted as described or that the irregularities in the nylon being used for the test were caused by chemical differences. Incidentally, Peters and Turner [11] make a point of emphasising that their dyebath conditions were not selected to give any particular degree of exhaustion.

We have knowledge of bulk dyeings which, broadly, confirm our conclusions.

Obviously, whether the fabric is commercially acceptable or not depends, as explained, on the cause of the irregularities in the nylon yarn. Yarn manufacturers now agree that chemical differences are becoming increasingly rare, and on this basis it is a fair conclusion that, no matter what the ultimate degree of irregularity found on dyeing at 130°c. under the preferred conditions, more uniform dyeings are obtained than on dyeing at 95°c.

Dr. G. H. LISTER: Would the lecturers summarise the method they would recommend for controlling exhaustion of the dyebaths in the region of 80%? In our opinion, while the control of exhaustion in medium and full depths may not be too difficult, to obtain such control in pastel colours, where unlevel dyeing is usually worst, would be a matter of extreme difficulty, requiring either high pH or high concentrations of "blocking" agents.

Mr. SEAMAN: Suggested pH values for the application of acid dyes to nylon have been published [6]. Under these conditions complete exhaustion is not obtained with the vast majority of dyes, even when dyeing pale colours. We agree, however, that with certain types of nylon, particularly 6-nylon, difficulties may arise, and more alkaline conditions or high concentrations of blocking agent may be required. Nevertheless, these conclusions do not apply to the vast majority of dyeings on 6,6-nylon. It should be remembered that, with very pale colours, there is not the same necessity for using acid dyes, as adequate wet fastness can normally be obtained with disperse dyes.

Mr. W. BEAL: If textile chemicals are used to restrict the exhaustion to approx. 80%, is the same improvement in levelling still obtained as if this exhaustion were achieved merely by pH control?

Mr. HADFIELD: A general answer to this question cannot be given. It is the authors' opinion, however, that, provided the auxiliary products possess the property of rapidly diffusing through nylon and provided they can buffer the exhaustion,

then they can be used to achieve the same results as suggested with pH control. Such auxiliary products, for use with level-dyeing acid dyes, are known. In the case of acid milling dyes, which require much more complex molecules, there are difficulties. The type of products which buffer the exhaustion with acid milling dyes normally possess very slow diffusion rates into the nylon, and, if these agents are absorbed in an uneven manner, they themselves can produce unlevelness. For this reason, pH control is preferred with acid milling dyes.

General Discussion on Colloquium Papers

Mr. W. H. JONES: Has any member of the panel had any experience of the use of lower pH values, which, the American literature suggests, gives increased uptake and better dyeings of disperse dyes on Terylene?

Mr. HADFIELD: An investigation of the dyeing of Terylene with disperse dyes under slightly acidic conditions has shown [1] that, with certain dyes, e.g. Dispersol Fast Yellow A (C.I. Disperse Yellow 1), an increase in the dyebath pH above 7 results in a decrease in exhaustion at high temperature. With this type of dye it is therefore advantageous to ensure that no alkalinity develops during dyeing, so that an acid buffer can be employed with advantage. With the vast majority of disperse dyes, however, no improvement is obtained by using a slightly acidic dyebath.

Mr. H. W. PARTRIDGE: In view of the susceptibility of nylon to damage by oxidising agents, has Mr. Hadfield examined the strength of nylon yarn which has been afterchromed at 130°C.?

Mr. HADFIELD: No experiments have been done to determine the effect of chroming at 130°C. on the tensile strength of nylon, since we do not consider that, with the chroming conditions recommended, serious damage will result. In any case, in the majority of instances the advantages of chroming at higher temperatures can be realised at lower temperatures than 130°C., e.g. 110°C.

Under these conditions, compared with chroming at 95°C., the effect on the tensile properties of the yarn will be very slight.

Dr. C. M. WHITTAKER: In discussing high-temperature machines, none of the authors has mentioned that this type of machine is equally successful in giving level results with aggregated dyes on the wool fibre, which is the most uneven dyeing fibre, owing to its dye affinity varying from root to tip.

Mr. SMITH: When applied to wool at ordinary temperature, some of the aggregated dyes will cover differences between root and tip very well. Others give a wide difference in colour, and as they migrate very little at the boil, a rise of temperature gives better migration and hence more level results. This high-temperature dyeing has to be done very carefully and for a short time only, or the wool fibre will be badly damaged; though if these dyes are unevenly applied on a cheese or a cone of yarn, as distinct from root-and-tip unevenness, I doubt whether sufficient migration will be obtained in the short time allowed to level out.

[1] Fern, A. S., J.S.D.C., 71, 508 (1955).

Mr. CLIFFORD PAINE (*President of the Society*) formally closed the Symposium by thanking all who had worked to make the Symposium a success.

COMMUNICATIONS

Studies on Aminoanthraquinone Compounds
I— Absorption Spectra in Solution and in the Solid State

G. S. EGERTON and A. G. ROACH

The ultraviolet and visible absorption spectra of six aminoanthraquinones have been determined in solution, on polymer films, and as solid deposits on quartz. The compounds were 1- and 2-amino-, 1:4- and 1:5-diamino-, 1:4:5-triamino-, and 1:4:5:8-tetra-amino-anthraquinone. The solvents were ethyl and *iso*propyl alcohols, and transparent polymer films of nylon, *N*-methoxymethylnylon, and secondary cellulose acetate were used. The effect of the solvent or substrate on the absorption spectrum and the problem of colour and chemical constitution in relation to the aminoanthraquinones have been discussed.

Introduction

Of the many thousand synthetic dyes available at the present time many of the most important are derivatives of anthraquinone. The introduction of substituent groups into the anthraquinone nucleus produces marked changes in colour, and the resultant products possess in general a marked degree of chemical stability. Two important classes of dyes which may be produced are the disperse dyes for the dyeing of the cellulose acetates and the synthetic fibres, such as nylon, and vat dyes for the dyeing of cellulosic fibres. The disperse dyes that result are in the main simple derivatives of aminoanthraquinone compounds, and the vat dyes benzoyl or more complex derivatives of the amino compounds. Thus 1:4-di- and 1:4:5:8-tetra-aminoanthraquinone are used commercially as disperse dyes (C.I. Disperse Violet 1 and C.I. Disperse Blue 1), and the benzoyl derivatives of 1:4-di-, 1:5-di-, and 1:4:5-tri-aminoanthraquinone have found application as vat dyes (C.I. Vat Red 42, C.I. Vat Yellow 3, and C.I. Vat Red 19)[1].

The photochemistry of the disperse and vat dyes when present on textile substrates is undoubtedly complex, and as a first step in an investigation of this problem it seemed desirable to consider the behaviour of the simple aminoanthraquinone compounds. It was decided to investigate the permanent changes produced by the action of light on transparent polymer films dyed with these compounds and to follow the changes spectrophotometrically. Since with any particular compound the spectrum depends upon the substrate (or solvent), it was desirable first to determine the spectra of highly purified aminoanthraquinone compounds and to consider the variations in the spectra produced by change in substrate and by change in chemical constitution.

Experimental

MATERIALS

Aminoanthraquinone Compounds

Commercial samples were extracted in a Soxhlet apparatus with ethyl alcohol for several hours, and the extract was filtered hot and allowed to crystallise in the dark. The process was repeated 4–6 times, using the crystals obtained from the previous crystallisation as the charge in the extraction thimble for the next stage. The final crystals were washed with ethyl alcohol and dried

in vacuo at room temperature. Details are given in Table I of some of the properties of the original sample and the purified compound after the final crystallisation.

TABLE I

Amino-anthra-quinone (Position of NH$_2$)	No. of Crystal-lisations	Melting Point (°c.) Original	Final	Nature of Crystals
1	4	253	252	Small red
2	5	303	304	Fine reddish-orange needles
1:4	4	266	269	Dark violet-red with metallic cast
1:5	4	316	319	Small red needles of high lustre
1:4:5	6	256	258	Long violet-blue with metallic cast
1:4:5:8	5	320	330	Long blue-black plates

Solvents

Ethyl and *iso*propyl alcohols were purified to spectroscopic purity.

Polymer Films

Nylon film (0·004 in. thick) was obtained from E. I. du Pont de Nemours Inc.; it was based upon the hexamethylenediamine–adipic acid polymer, and was free from plasticiser. *N*-Methoxymethylnylon film (0·002 in. thick) also was free from plasticiser, and was supplied by Imperial Chemical Industries Ltd. Secondary cellulose acetate film (0·001 in. thick) was obtained from British Celanese Ltd., and was freed from plasticiser by repeated extraction in cold ethyl alcohol extending over several weeks. The other two types of film also were soaked in cold ethyl alcohol for 1 hr. to remove any surface contamination.

DYEING OF POLYMER FILMS AND PREPARATION FOR

ABSORPTION

Measurement

Solutions of the purified aminoanthraquinone compounds in ethyl alcohol were used to dye the polymer films in level colours at temperatures ranging from 25° to 50°c. Smooth dyed and undyed polymer films suitable for spectrophotometric examination were prepared by washing the film

(after alcohol treatment) with repeated changes of cold and warm distilled water, and then rolling it flat on to a clean glass plate and securing the edges of the film, which was then allowed to dry at room temperature. Absorption spectra of the dyed films were measured in comparison with those of the undyed films, the cut-off wavelengths of the latter being 225, 245, and 250 mμ. for cellulose acetate, N-methoxymethylnylon, and nylon films respectively. The spectra were measured on a Unicam SP 500 quartz spectrophotometer.

Solid Films on Quartz

Thin transparent films of the six aminoanthraquinones were deposited in vacuo on quartz plates using the Model 6E coating unit of Edwards High Vacuum Ltd. The operating conditions were varied slightly with each compound to produce the most satisfactory deposition.

Results

1-AMINOANTHRAQUINONE

The absorption maxima of this compound in solution and in the solid state are given in Table II. Some data are recorded from the literature for solutions in dioxan, hexane, o-chlorophenol, and methyl alcohol, and the remainder have been determined experimentally.

TABLE II
1-Aminoanthraquinone

Solvent or Substrate			Wavelength	of	Absorption Maxima (mμ.)*		
Dioxan [3]	—	245	(270)	305	468
Methyl alcohol [3] ...	—	236	(270)	298	475
Ethyl alcohol	—	243	273	310	475
isoPropyl alcohol ...	—	243	273	310	480
n-Hexane [4]	—	245	275	295	445
o-Chlorophenol [3]	—	—	—	—	488
Secondary cellulose acetate	—	245	272	308	470
Nylon	—	—	273	312	490
N-Methoxymethylnylon	—	—	275	312	482
Solid film on quartz ...	210	245	—	318	490

* Major inflection points are indicated in parentheses.

In the range covered in the ultraviolet region there seem to be three main band systems, two of less intensity at 270–275 mμ. and 295–318 mμ., and the third of very marked intensity at 236–245 mμ. Because of the strong absorption of undyed nylon and N-methoxymethylnylon films in the latter region, this third band could not be observed on the dyed nylon-type films. There may also be a fourth absorption band of high intensity in the region of 210 mμ., but it was possible to observe this band only with the solid film on quartz. One of the most notable characteristics of the aminoanthraquinones deposited on quartz is the sharpness of the bands in the ultraviolet region compared with the wide spread of the visible absorption bands.

The absorption spectrum of 1-aminoanthraquinone on cellulose acetate film is somewhat similar to that found in dioxan solution. In polar solvents, such as o-chlorophenol, there is a bathochromic shift of the visible band similar to that

which occurs with the dyeings on the two nylon-type films and with the solid dye film on quartz.

2-AMINOANTHRAQUINONE

The absorption maxima of this compound in solution and in the solid state are given in Table III. The intense ultraviolet band shown by 1-aminoanthraquinone at just below 250 mμ. is present in the 2-amino compound, but the minor bands in the former compound around 275 and 310 mμ. are replaced by another intense band in the neighbourhood of 300 mμ. With 2-aminoanthraquinone there is also an inflection which is not very well defined and somewhat indefinite in location between 325 and 340 mμ. The results with the solid film on quartz suggest that, as with the 1-substituted derivative, there is an absorption band around 200 mμ., but in this case slightly below rather than above this wavelength.

TABLE III
2-Aminoanthraquinone

Solvent or Substrate	Wavelength	of	Absorption (mμ.)		Maxima
Dioxan [3]	248	281	295	(325)	422
Methyl alcohol [3]	242	(286)	298	(327)	440
Ethyl alcohol ...	243	—	298	(335)	452
isoPropyl alcohol	243	—	302	(335)	460
n-Hexane [4] ...	235	287	—	325	430
o-Chlorophenol [3] ...	—	—	—	—	445
Cellulose acetate...	243	—	300	(330)	433
Nylon	—	—	302	(337)	462
N-Methoxymethyl-nylon ...	247	—	303	(342)	460
Solid film on quartz	240	—	300	(337)	455

The absorption band around 300 mμ. is particularly well defined on the polymer films, just as it is in solution in ethyl or isopropyl alcohol. The absorption spectrum of this compound on nylon film is remarkably similar to that of the solution in isopropyl alcohol. The definition of the visible band with the solid film on quartz is not good and compares unfavourably with the sharpness of the bands in the ultraviolet region. However, it is difficult to produce completely satisfactory films of this compound by vacuum deposition on quartz. On the solid substrates there is a general bathochromic shift in the higher-wavelength bands in the order— cellulose < acetate < quartz < N-methoxymethylnylon < nylon.

1:5-DIAMINOANTHRAQUINONE

Comparison of the absorption maxima quoted in Table II for 1-aminoanthraquinone with similar data given in Table IV for the 1:5-diamino compound shows quite a close similarity between the position of the band systems of the two compounds, although there are differences in intensity and definition. The short-wavelength band is still very intense, but its position is slightly lower at approx. 230 mμ. in the diamino compound. The band at 275 mμ. is now much more strongly defined, but that at 310 mμ. is slightly lower in wavelength and is now a somewhat indefinite inflection (except with the solid film on quartz).

TABLE IV
1:5-Diaminoanthraquinone

Solvent or Substrate	Wavelength	of	Absorption	Maxima	(mμ.)
Dioxan [2]	—	275	—	482	
Methyl alcohol [5] ...	—	—	—	487	—
Ethyl alcohol ...	232	278	(297)	493	—
*iso*Propyl alcohol	232	278	(297)	492	—
o-Chlorophenol [3] ...	—	—	—	500	—
Cellulose acetate...	230	277	(297)	487	—
Nylon	—	280	(302)	497	—
N-Methoxymethyl-nylon	—	280	(302)	495	—
Solid film on quartz	242	—	306	507	(540)

Although the spectra of this compound on the polymer films are similar in general to those in ethyl or *iso*propyl alcohol solution, there is a marked divergence from the spectra of the solid film on quartz. In the latter case the absorption band around 230 mμ. in solution or on cellulose acetate is displaced to about 242 mμ., the band at around 280 mμ. is absent, and a new band, which is possibly a development of the inflection observed in solution at this wavelength region, is found at 306 mμ. In the visible region, apart from a batho-chromic displacement of the band found in solution, the solid film on quartz shows evidence of an inflection in the neighbour-hood of 540 mμ. This seems to be the only case in which two bands are shown in the visible region with this compound, and in view of the existence of twin peaks with the 1:4 isomer, it is possible that these observations are significant.

1:4-DIAMINOANTHRAQUINONE

Although the introduction of a second amino group into the 5 position of the molecule of 1-aminoanthraquinone pro-duces only minor changes in the character of the absorption spectrum, its introduction in the 4 position results in major changes, which are most evident in the visible region. The single visible absorption band of the 1 and 1:5 compounds is split into two bands of nearly equal intensity, and there is the appearance of an inflection on the shorter-wavelength side of the twin peaks

TABLE V
1:4-Diaminoanthraquinone

Solvent or Substrate	Wavelengths	of	Absorption	Maxima	(mμ.)		
Methyl alcohol [5,6]	—	—	—	(515)	550	590
Ethyl alcohol ...	(237)	251	(297)	(522)	556	595
*iso*Propyl alcohol	(235)	249	(300)	(527)	555	595
n-Hexane [6]	—	—	—	(500)	535	575
o-Chlorophenol [3] ...	—	—	—	—	554	596
Quinoline [6]	—	—	—	(520)	560	598
Cellulose acetate ...	(235)	250	(293)	(520)	550	590
Nylon	—	—	—	(305)	(542)	562	602
N-Methoxymethyl-nylon	—	—	—	(300)	(530)	562	601
Solid film on quartz	210	258	(305)	—	550	—

(Table V and Fig. 1). The position of the twin peaks depends upon the nature of the solvent or substrate. In the non-polar solvent *n*-hexane the wavelengths are at a minimum (535, 575 mμ.), whereas in quinoline or *o*-chlorophenol these bands are located at wavelengths about 20 mμ. greater. On the polymer films the bands lie between those for the polar and non-polar solvents with cellulose acetate, and rather closer to the polar solvents with the two nylon-type films. There is again quite a close similarity between the spectrum of the dyed cellulose acetate film and that of the solution in *iso*propyl alcohol.
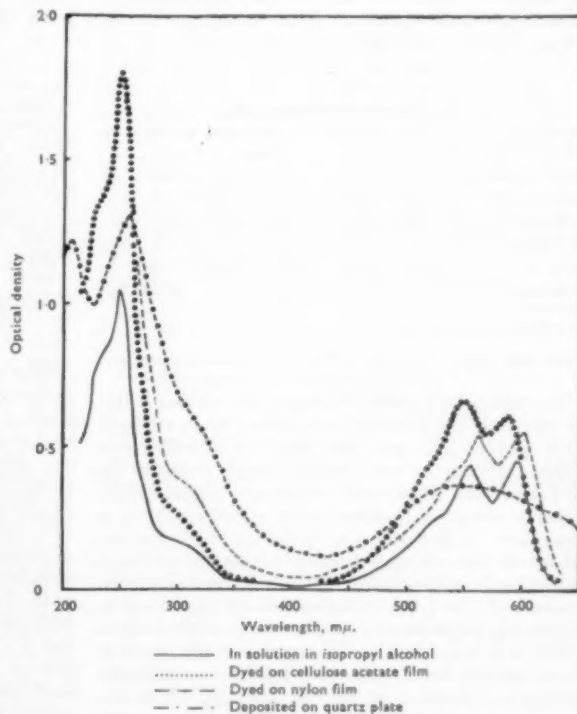
FIG. 1— Absorption Spectrum of 1:4-Diaminoanthraquinone

In the ultraviolet region the intense peak around 250 mμ. is still in evidence, but there is now the appearance both in alcohol solution and on the cellulose acetate film of an inflection around 235 mμ., which is not evident with the 1 and 1:5 compounds. There is also no absorption band around 280 mμ. with the 1:4 derivative, although the inflection just above 300 mμ. is still present.

The solid film on quartz is mainly notable for the absence of the twin peaks in the visible region. Although there is the possibility of a somewhat indefinite inflection above 600 mμ., there is a marked contrast with the spectra in solution or on the polymer films. In the ultraviolet region the band at 210 mμ. observed with the solid film of 1-aminoanthraquinone is again observed. Sheppard and Newsome [6] have measured the visible

absorption spectrum of 1:4-diaminoanthraquinone in the vapour phase at 195°c., and under those conditions the twin-peak system is apparently replaced by a general absorption band.

1:4:5-TRIAMINOANTHRAQUINONE

The absorption maxima of this compound in solution and in the solid state are given in Table VI. In some respects the spectrum of this compound may be regarded as a composite of those of the 1:4- and 1:5-diamino compounds. Thus, the high-intensity band of 1:4:5-triaminoanthraquinone in the ultraviolet region is intermediate in position between the corresponding peaks of the 1:4 and 1:5 isomers. In solution in *iso*propyl alcohol the band maxima occur at 232 mμ. (1:5), 238 mμ. (1:4:5), and 249 mμ. (1:4).

TABLE VI
1:4:5-Triaminoanthraquinone

Solvent or Substrate	Wavelength of Absorption Maxima (mμ.)					
Methyl alcohol [a] ...	—	—	—	—	561	601
Ethyl alcohol ...	237	(260)	(290)	(535)	570	610
*iso*Propyl alcohol	238	(262)	(293)	(538)	568	607
Cellulose acetate ...	—	262	(*)	(*)	561	602
Nylon	—	266	(292)	(537)	574	617
N-Methoxymethyl-nylon	—	—	—	—	575	616
Solid film on quartz	240	—	—	—	545	—

* These inflections are somewhat indefinite and uncertain of location.

The inflection around 300 mμ. observed with the 1:4 and 1:5 compounds is retained at a slightly lower wavelength, and the band at 275–280 mμ. in the 1:5-diamino compound, which is absent in the 1:4 isomer, apparently reappears in the 1:4:5-triamino compound, either as an inflection or as a minor peak, at 260–266 mμ. In the visible region the spectra of the 1:4 and 1:4:5 compounds are very similar, and in the case of the latter compound the influence of the 1:5 constituent on the spectrum is apparently suppressed by the more powerful effect of the 1:4 constituent. Compared with the 1:4 compound the twin peaks of 1:4:5-triaminoanthraquinone in solution or on the polymer films are displaced in the same regular progression about 10–15 mμ. to higher wavelengths. On cellulose acetate and N-methoxymethylnylon films there seems to be a new inflection between 440 and 450 mμ.

The spectrum of the solid film on quartz again fails to reveal the presence of twin peaks in the visible region, although there appears to be an inflection in the region of 610–640 mμ.

1:4:5:8-TETRA-AMINOANTHRAQUINONE

Although the colour (royal blue) of solutions of this compound is markedly different from those of solutions of 1-aminoanthraquinone (yellowish orange) and of 1:5-diaminoanthraquinone (reddish orange), in the ultraviolet region there are marked similarities between the spectra of all three compounds (Table VII). The intense band near 250 mμ., the weaker band around 275 mμ., and the inflection just above 300 mμ. are all in evidence.

In the visible region the influence of 1:4 substitution predominates, and except with the solid film on quartz the twin peaks are observed. However, unlike the 1:4 and 1:4:5 compounds, 1:4:5:8-tetra-aminoanthraquinone is distinguished by changes in the relative size of the twin peaks, so that in solution in *iso*propyl or ethyl alcohol the band at lower wavelength becomes an inflection rather than the well defined peak that is observed on cellulose acetate film. On nylon film the band is somewhat intermediate between its states in solution and on the acetate film. The inflection which is found on the lower-wavelength side of the twin peaks with the 1:4:5-triamino compound seems to be absent with the 1:4:5:8 compound both in solution and on the polymer films.

TABLE VII
1:4:5:8-Tetra-aminoanthraquinone

Solvent or Substrate	Wavelength of Absorption Maxima (mμ.)				
Methyl alcohol [a] ...	—	—	—	600	629
Ethyl alcohol ...	240	273	(310)	(607)	635
*iso*Propyl alcohol...	240	273	(310)	(607)	635
Cellulose acetate ...	—	273	(308)	602	648
Nylon	—	277	(307)	615	656
N-Methoxymethyl-nylon ...	—	—	—	595	655
Solid film on quartz	243	—	—	595	—

GENERAL COMMENTS

The absorption spectra of the six aminoanthraquinones are very similar for solutions in *iso*propyl alcohol and for solutions in ethyl alcohol. A recent paper by Moran and Stonehill [7] has recorded the absorption maxima for solutions of four of these compounds in the latter solvent. Their results for the 1:4- and 1:5-diamino compounds are in substantial agreement as regards the main absorption bands, but these authors record a number of inflections (at 255, 266, 288, and 408 mμ. with 1:4-diaminoanthraquinone, and at 239, 322, 410, and 440 mμ. with the 1:5 isomer) which it has not been possible to detect in the present investigation. With 1:4:5-triaminoanthraquinone Moran and Stonehill report an inflection in the low-absorbing region at 410 mμ., which also has not been found. The position of the twin peaks is recorded by these workers at lower wavelengths than those in Table VI, the far absorption band being apparently an inflection in their observations. With 1-aminoanthraquinone the divergencies between these authors' results and those recorded in this paper and elsewhere are more marked. In the visible region, inflections are recorded by Moran and Stonehill at 406 and 478 mμ. and a band at 497 mμ. There seems to be little indication from our own or other sources of the two inflections, and the maximum of the main visible band is recorded in the literature at values ranging from 445 mμ. (hexane), 468 mμ. (dioxan), to 475 mμ. (methyl alcohol). The value of 497 mμ. therefore seems too high. One peculiar feature of the results of Moran and Stonehill is the common inflection at 406–410 mμ. with all the four compounds tested. In this region the absorption of these compounds is at a minimum, and it seems likely that instrumental

errors or impurities in the samples cannot be ruled out.

In the experimental section of their paper Moran and Stonehill state that the aminoanthraquinones were prepared by hydrolysis of the corresponding benzoylated dyes with boiling sulphuric acid, and recrystallisation from alcohol. Whether this procedure is sufficient for complete purification of these compounds, in view of the difficulty of purifying the benzoylated aminoanthraquinones, is open to question, but the presence of some of the amine as the acid salt might well have the effect of displacing the visible absorption band of 1-aminoanthraquinone and repressing (and displacing) one of the twin peaks in the 1:4:5-triamino compound.

Their remark that photochemically active (anthraquinone) vat dyes dried in contact with cellulose or extracted in cellulose thimbles caused the latter to disintegrate also suggests that some of the dyes were not completely free from acid. It is difficult to wash vat dyes, which have been dissolved in concentrated sulphuric acid and then precipitated with water, completely free from acid. If the acid-contaminated precipitate is dried in the presence of filter paper, the residual acid carbonises the cellulose, as might be expected, but in the complete absence of acid, vat dyes can be dried in contact with cellulose without decomposition of either substance, as is evidenced by the vast quantities of these dyes which have been used successfully by the textile industry.

Comparison of Spectra

COLOUR AND MOLECULAR STRUCTURE

The colour of an organic compound is generally attributed to the presence in the molecule of chromophoric and auxochromic groups. For the aminoanthraquinone compounds the chromophore is represented by the anthraquinone nucleus and the auxochrome by the amino group. The latter is a saturated group with a strong electron-donating ability, and the absorption characteristics of aminoanthraquinone compounds can, therefore, be attributed to the resonance hybrid exhibiting a greater contribution from the extreme ionic forms. For 1-aminoanthraquinone the ionic form would be of the type I and for 2-aminoanthraquinone of the type II. The electron-donating ability of the

amino group can thus increase the contribution made by the ionic forms by a mesomeric shift of the electrons from the amino group initially to the ring and subsequently to the oxygen atom (III and IV). Because of the greater distance involved in this electron shift with the 2-amino compound, substitution in this position results in the introduction of the least amount of colour.

The basic molecular unit of the aminoanthraquinone compounds can be considered to be *p*-benzoquinone, which is itself a chromophore in which the centres of unsaturation are joined by a system of conjugated double bonds. The symmetrical addition, initially of one benzene ring, and subsequently of a further ring, increases the length of the conjugated system and the number of possible resonance structures, so that the chromophoric power in substituted derivatives increases in the order— *p*-benzoquinone < *α*-naphthaquinone < anthraquinone. This addition of benzene rings modifies the absorption spectrum of *p*-benzoquinone in both the ultraviolet and visible regions of the spectrum (Table VIII). The change of colour in the parent compounds was attributed by Morton and Earlam[8] to a reduction in quinonoid character as a result of the introduction of the benzene rings. The oxidation–reduction potential of the quinone decreases in the same order.

TABLE VIII
Absorption Maxima in Dioxan Solution[8]

Compound		Wavelength[a] (mμ.)			
p-Benzoquinone ...	238	—	286	—	455
α-Naphthaquinone ...	249	—	—	327	(420)
Anthraquinone ...	251	(265)	(275)	323	(400)

[a] Major inflection points are indicated in parentheses.

Some attempts have been made to construct the absorption spectrum of anthraquinone qualitatively from simpler compounds by a method of summation. Thus Spruit[9] postulated the anthraquinone spectrum to be double that of *α*-naphthaquinone, whilst Morton and Earlam[8] derived the spectrum from twice that of acetophenone plus a contribution from *p*-benzoquinone.

The amino group has found wide use as an auxochrome and in common with other groups, such as NH·Alk, is capable of salt formation. The introduction of an auxochrome into a chromophore can be expected to lead to changes in both the ultraviolet and visible regions of the spectrum. The extent of this modification will depend upon the position of substitution and the number of groups introduced. This is clearly shown by the results described.

Aggregation, steric hindrance, and hydrogen bonding are other factors which may also modify the absorption spectrum. The effect of steric hindrance has been observed for alkyl- and aryl-substituted amino groups[3], but would not seem to be significant for the unsubstituted derivatives. The formation of the bridge O··H–N in aminoanthraquinones must be considered a possibility, and Astbury *et al.*[10] have shown that such hydrogen bonding will modify the infrared
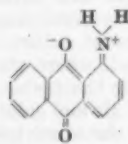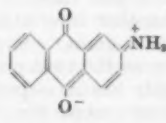
(I)   (II)
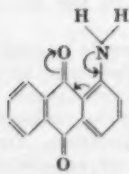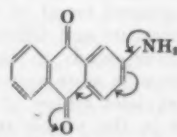
(III)   (IV)

spectra of amides. The amount of energy associated with hydrogen bonding is small [11], and it is therefore possible that in some photochemical processes this may be the first bond to be broken.

Intramolecular hydrogen bonding of the type V is possible where there is an amino group in one or more of the 1, 4, 5, and 8 positions, but for substitution in the 2, 3, 6, and 7 positions hydrogen bonding must be limited to the intermolecular type because of spatial considerations. The results of Flett [12] suggest that the hydrogen bonding present in hydroxy derivatives of anthraquinone is stronger than that in the amino compounds.

(V)
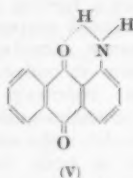
The absorption spectra of aminoanthraquinone compounds seem to fall into two main types, depending upon whether the initial substitution is in the 1 or the 2 position. There is a wide variation in absorption with the diamino compounds. Thus the spectrum of 1:5-diaminoanthraquinone resembles that of 1-aminoanthraquinone, with a higher absorbance for the diamino compound, particularly in the visible absorption band. Spruit [9] has shown that the intensity of the visible absorption band of 1:5-dihydroxyanthraquinone is approximately twice that of the corresponding band of the 1-hydroxy compound. A similar relation has been observed for the corresponding amino derivatives by Peters and Sumner [3]. These observations relate to the band in the visible region, where we have observed a similar ratio for solutions in isopropyl alcohol, but in the ultraviolet the ratio between the bands seems to be nearer unity. This would seem to suggest that the introduction of an auxochrome into a chromophore does not necessarily influence the absorption in the ultraviolet region as much as it does in the visible region.

Whereas only one visible absorption band is observed with 1:5-diaminoanthraquinone, the 1:4 isomer is characterised by twin peaks of somewhat similar intensity. Polyamino compounds substituted in the 1 and 4 positions show the same effect. Allen et al.[13] suggested that the electrons of the two amino groups undergo a mesomeric shift initially to the ring and subsequently to the oxygen atom (VI). As a result of this electron drift the contribution from the ionic form (VII) to the resonance hybrid is increased, and twin peaks are formed.

(VI)   (VII)
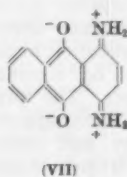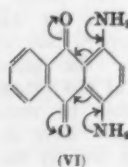
In certain circumstances it appears that these twin peaks can be suppressed. Thus Peters and Sumner [3] observed their suppression when the hydrogen atoms of the amino groups in 1:4-diaminoanthraquinone were replaced by electron-attracting groups such as acetyl or benzoyl. Such groups would be expected to reduce the mesomeric shift of electrons to the anthraquinone nucleus, and there would thus be a reduction in the contribution of the ionic forms to the resonance hybrid. The addition of hydrochloric acid to a methyl alcohol solution of 1:4-diaminoanthraquinone also results in the replacement of the twin peaks by a general absorption band with a maximum at lower wavelengths, owing to the formation of the monohydrochloride and the suppression of the effect of one of the amino groups [3].

The absorption character of 1:8-diaminoanthraquinone appears to be intermediate between those of the 1:4 and 1:5 isomers. Although maximum absorption with the 1:8 isomer occurs in the same wavelength region as for the 1:5-diamino compound, the absorption spectrum is characterised by twin peaks of lower definition but similar to those observed for the 1:4 isomer. Thus, Hartmann and Lorenz [2] find that in dioxan solution 1:8-diaminoanthraquinone exhibits absorption maxima at 458 mμ. and 490 mμ. with an inflection at 435 mμ.

EFFECT OF SUBSTRATE

When a comparison is made of the absorption spectra of the aminoanthraquinone compounds upon the different polymer films it is found that, although the type of film does not change the absorption character of a particular compound, it does influence the wavelength of maximum absorption. In the visible region the absorption maxima exhibit a general bathochromic shift in the order— cellulose acetate $<$ N-methoxymethyl-nylon $<$ nylon. The absorption spectra of the monosubstituted aminoanthraquinones and the 1:5-diamino compound are similar in isopropyl alcohol solution and on N-methoxymethylnylon. There is a smaller degree of similarity with the corresponding dyeing on nylon or with the dye film on quartz. With the polyamino compounds with substitution in the 1 and 4 positions the spectra in isopropyl alcohol are rather more comparable with those of the dyed cellulose acetate films. Another interesting point occurs with the 1:4:5:8-tetra-amino compound, where the separation between the twin peaks in the visible region is appreciably less in isopropyl alcohol solution than on cellulose acetate film. In the ultraviolet region the spectra of the 1:4, 1:4:5, and 1:4:5:8 derivatives become increasingly similar to that of 1-amino-anthraquinone, with increase in the number of amino groups.

The general trend of the results suggests that the similarities and differences between the various amino compounds in the different states are in some respects more apparent in the visible than in the ultraviolet region of the spectrum. Since the changes in the visible region are associated with the development by the amino group auxochrome

of the potential colour bands of the chromophore in this spectral region, this is not unexpected. The ultraviolet absorption spectrum is more characteristic of the optical properties of the chromophore, which are of a complex nature.

The changes in the visible absorption spectrum manifest the variation in colour produced by the introduction of one or more amino groups, ranging from the pale yellow of 2-aminoanthraquinone to the royal blue of the 1:4:5:8 compound. There is thus a general bathochromic shift in the order— 2-amino $<$ 1-amino $<$ 1:5- and 1:4-diamino $<$ 1:4:5-triamino and 1:4:5:8-tetra-amino, which can be attributed to the effect of the amino group on the absorption of the chromophore, and an increase in the ability of the amino group to enhance the contribution of the ionic form.

In the ultraviolet region the changes in absorption as a result of amino group substitution are somewhat difficult to interpret. The high-intensity band in the region of 250 mμ. appears to characterise the aminoanthraquinone compounds and is comparable with the band observed for both a-naphthaquinone and anthraquinone. The absorption spectra of 1-amino- and 1:5-diaminoanthraquinone resemble one another to some extent, and of these two compounds the spectrum of the mono compound is rather more similar to that of anthraquinone, the bands at 275 mμ. and 310 mμ. being more sharply defined with the amino compound. There is some similarity between the absorption spectra of 1:5-diaminoanthraquinone and p-benzoquinone. This may be the result of substitution in the 1 and 5 positions increasing the contribution of the system at the expense of that of the benzene, so that a mesomeric shift of electrons from the two amino groups to the carbonyl groups is favoured. Where only one amino group is present, a mesomeric shift is possible to only one carbonyl group, so that the contribution of the benzene rings to the absorption spectrum would not be expected to be suppressed. The bathochromic shift observed with 1:4-di-, 1:4:5-tri-, and 1:4:5:8-tetra-aminoanthraquinone is probably the result of the mesomeric drift of electrons to both the ring and the oxygen atom of the carbonyl group, the drift increasing with the number of amino groups introduced. The ionic forms would thus exert a greater influence on the optical properties of the hybrid. The similarity of the absorption spectra of p-benzoquinone and 2-aminoanthraquinone is not unexpected, since a mesomeric shift of electrons from the amino group to the ring would be expected to depress the modifying influence of the benzene ring carrying the substituent on the absorption spectrum.

There are some interesting features about the results obtained for the solid films deposited on quartz. In general, there is a similarity between these spectra and those obtained in solution or on polymer films. The predominant feature of the films on quartz is an absorption band in the region of 240–260 mμ.; there is a similar band in solution. A new band around 210 mμ. is also observed with 1-amino- and 1:4-diamino-anthraquinone. In this range the absorbance of the other substituted compounds increases markedly with reduction in wavelength, indicating an absorption band just below 200 mμ. In the visible region the most interesting feature is the suppression of the twin peaks shown by compounds substituted in the 1 and 4 positions. The twin peaks found in solution are replaced by a general absorption band covering the same wavelength range. There is, however, some evidence of a slight inflection at the longer-wavelength end of the band. Sheppard and Newsome[6] measured the visible absorption spectrum of 1:4-diaminoanthraquinone in the vapour phase. At low temperatures the spectral definition was poor, but it improved with rise in temperature, and at 195°c. the spectrum of the vapour resembled that obtained for the compound deposited as a thin film on quartz. There was a general absorption band with an inflection at the longer-wavelength end. It is probable that the bathochromic displacement of the visible absorption bands of the aminoanthraquinone compounds in the solid state is the result of intermolecular bonding, such as has been postulated by Weinstein and Wyman[14] to be responsible for a similar change in the spectra of Indigo and its derivatives in the solid state. The light stability of these compounds is also appreciably affected by the presence of these intermolecular bonds, as will be described in a subsequent contribution in this series.

*   *   *

DEPARTMENT OF TEXTILE CHEMISTRY
   FACULTY OF TECHNOLOGY
      UNIVERSITY OF MANCHESTER

References

[1] Society of Dyers and Colourists and American Association of Textile Chemists and Colorists, *Colour Index* (Bradford and Lowell, Mass.: 2nd edition 1956).

[2] Hartmann, H., and Lorenz, E., *Z. Naturforschung*, **7a**, 360 (1952).

[3] Peters, R. H., and Sumner, H. H., *J.C.S.*, 2101 (1953).

[4] Lauer, K., and Horio, M., *J. prakt. Chem.*, **145**, 273 (1936).

[5] Peters, R. H., and Sumner, H. H., *J.S.D.C.*, **72**, 77 (1956).

[6] Sheppard, S. E., and Newsome, P. T., *J. Amer. Chem. Soc.*, **64**, 2937 (1942).

[7] Moran, J. J., and Stonehill, H. I., *J.C.S.*, 765 (1957).

[8] Morton, R. A., and Earlam, W. T., *ibid.*, 159 (1941).

[9] Spruit, C. J. P., *Rec. Trav. chim.*, **68**, 325 (1949).

[10] Astbury, W. T., Dalgliesh, C. E., Darmon, S. E., and Sutherland, G. B. B. M., *Nature*, **162**, 596 (1949).

[11] Pauling, L., *The Nature of the Chemical Bond* (New York: Cornell University Press, 1945), p. 284.

[12] Flett, M. St. C., *J.C.S.*, 1441 (1948).

[13] Allen, C. F. H., Wilson, C. V., and Frame, G. F., *J. Org. Chem.*, **7**, 169 (1942).

[14] Weinstein, J., and Wyman, G. M., *J. Amer. Chem. Soc.*, **78**, 2387 (1956).

Studies on Aminoanthraquinone Compounds
II— Photochemistry of Dyed Polymer Films

G. S. EGERTON and A. G. ROACH

A study has been made of the action of near ultraviolet radiation and visible light on transparent polymer films of cellulose acetate, nylon, and N-methoxymethylnylon dyed with six aminoanthraquinones (1- and 2-mono-, 1:4- and 1:5-di-, 1:4:5-tri-, and 1:4:5:8-tetra-aminoanthraquinone). The reaction was followed spectrophotometrically in a closed system of dry nitrogen or oxygen. The general feature of the exposures in oxygen is a decrease in optical density throughout the spectrum. This is particularly a feature with the 1- and 2-amino compounds. With the derivatives substituted in the 1 and 4 positions there is a reduction in the intensity of the twin peaks in the visible region, the rate of decrease being greater for the peak at longer wavelength, and in some cases a general absorption band replaces the twin peak system. The rate of fading of 2-aminoanthraquinone on nylon and cellulose acetate film is as great in nitrogen as in oxygen, although with 1:5-diaminoanthraquinone the rate is greater in oxygen. The light fastness of the aminoanthraquinones is greatest on cellulose acetate film, intermediate on nylon, and least on N-methoxymethylnylon. Among the six aminoanthraquinones the light fastness on a particular substrate is least with 2-amino- and 1:5-diamino-anthraquinone, and greatest with the 1, 1:4, 1:4:5, and 1:4:5:8 compounds. On exposure in nitrogen, but not in oxygen, of 1-amino- and 1:5-diamino-anthraquinone on N-methoxymethyl-nylon, a new peak around 400 mμ. is formed. Under the same conditions 2-aminoanthraquinone behaves differently.

Introduction

The change of colour that occurs when dyed textile fabrics are exposed to light is the result of a complex process, which is affected to a considerable extent by a large variety of factors, some of which under conditions of practical use are largely uncontrollable. Water vapour and oxygen present in the atmosphere, the chemical constitution of the dye, the textile substrate, the nature of the bond between the dye and the substrate, the aggregation of the dye, the quality of the radiation, temperature, impurities in the dye–polymer system, etc. are all factors which may influence the nature of the results very considerably [1]. It is owing to this complexity of the reactions involved that in only a few instances has it been possible to isolate and identify the photoproducts. The formation of oxidation products of indigo and its methyl derivative when dyeings of these compounds on cotton are exposed to light has been reported [2,3], as has the formation of phthalic acid and its anhydride by the action of light on anthraquinone compounds [4]. On the other hand, there appear to be instances where reduction of the dye occurs. Thus, Blaisdell [5] found that, when solutions of azo dyes in organic solvents are exposed to ultraviolet radiation, hydrazines and substituted aniline derivatives are formed.

In some cases the fading of dyes appears to be more rapid in the presence of oxygen [6,7], but other dyes appear to fade equally fast in nitrogen and air [8]. It is possible that the chemical constitution of the dye and the nature of the attachment of the dye to the textile polymer are important factors in determining whether the fading reaction proceeds by oxidation or reduction. An interesting investigation of the action of light on the disperse dye 1:4-bismethylaminoanthraquinone, dyed on nylon and secondary cellulose acetate fabric, has been reported by Couper [9]. A chromatographic technique was used to separate the fading products, which seemed to comprise a very complex mixture. The fading reactions were considered to include N-dealkylation, hydrolysis of amino (or methyl-amino) to hydroxy groups, oxidation of amino

to imino groups and of methylamino to methyl-imino groups, nuclear hydroxylation and de-amination, and possibly oxidation of amino to hydroxylamino groups and of methylamino to N-methylhydroxylamino groups.

A knowledge of the photochemistry of the simple aminoanthraquinones would be of advantage in the study of the fading of the more complex vat and disperse dyes derived from these parent compounds, and it therefore seemed advantageous to study the changes, produced by irradiation under standard conditions, in the absorption spectra of transparent polymer films dyed with highly purified aminoanthraquinone compounds. It does not follow, of course, that the same type of reactions will occur with less pure samples of dye, or with more complex derivatives of aminoanthraquinone, but the present technique offers an opportunity of studying the early stages of photochemical reaction before it is complicated by a multitude of fading products.

Experimental

Details of the aminoanthraquinone compounds and polymer films used in this work have already been given [10].

EXPOSURE CONDITIONS

During exposure to light and subsequent measurements of absorption spectra it was essential to maintain the films in a vertical position. Consequently, the films were mounted on frames constructed from silver wire, which fitted firmly inside standardised quartz cells (45 mm. × 10 mm. × 10 mm.). Crossbars across the centres of the top and the bottom of the frame provided support for the film. A brass top, containing both an inlet and an outlet tube for gases, was sealed with Apiezon W vacuum wax on to the open end of the quartz cell, after the silver frame with the appropriate mounted sample had been inserted. The inlet consisted of a small-diameter brass pipe which extended almost to the bottom of the quartz cell. Dry gas left the cell by an exit hole drilled in the top itself, and by this method the film was exposed to a continuous stream of dry gas

circulated round it. Throughout an experiment comprising exposure to light and measurement of absorption spectra the cells were contained in a standard cell-holder (with 3 cells per holder), the supply of gas being maintained continuously through the cell. Suitable modifications were made to the lid of the cell compartment in the Unicam spectrophotometer so as to enable the holder to be inserted in or removed from the compartment without in any way affecting the gas supply. The dyed films in quartz cells were always measured against the similarly exposed undyed film. Changes in the absorption spectra of the undyed films as the result of exposure to near ultraviolet radiation and visible light were slight and not sufficient to affect the nature of the results. Supplies of oxygen and nitrogen (oxygen-free) were obtained from cylinders, and were dried with phosphorus pent-oxide before use. The temperature of the gas and the cell was maintained constant (at 35°c.) during exposure, which was made through a Chance heat filter to a 400-watt high-pressure mercury-vapour lamp (Osram, G.E.C.). This glass-enclosed lamp emits intense lines in the near ultraviolet at 365 mμ. and in the visible region [11].

No change in the spectrum of the dyed film was observed when the dry gas was passed through the cell for 2500 hr. while the film was kept in the dark.

Discussion of Results

One of the most striking features of the results obtained by exposing polymer films dyed with aminoanthraquinone compounds to near ultra-violet radiation and visible light is that there is usually a decrease in absorbance at the main absorption bands. In some cases increases in absorption are encountered, but these are comparatively rare, except with dyeings on N-methoxy-methylnylon film exposed in dry nitrogen. The results for 1- and 2-aminoanthraquinone exposed on cellulose acetate film in dry oxygen are typical of the general type of results obtained (Fig. 1). With the 1-amino compound the absorption bands at 245 mμ. and in the visible region at 470 mμ. retain their general shapes even after 2500 hr. exposure, whereas the more weakly defined bands at 272 and 308 mμ. become inflections after this period. The 2-amino compound is much more rapidly affected by light than is the 1-substituted derivative. The two sharply defined ultraviolet peaks at 243 and 300 mμ. are rapidly reduced in intensity, and after 500 hr. exposure the latter band has lost its definition completely, although the former still possesses the general features of an absorption band. In the visible region there is a gradual decrease in the absorbance as exposure proceeds. The behaviour of these two compounds on nylon is somewhat similar to that on cellulose acetate: the 1-substituted derivative is more resistant to light, and there is a general decrease in absorption throughout the spectrum.

Moran and Stonehill [12] have given some details of the effects of the radiations from a Point-o-Lite arc on a dyeing of 1-aminoanthraquinone on cellulose

Time of Exposure (hr.)
——— 0
.... 1000
— — — 2500

A— 1-Aminoanthraquinone

Time of Exposure (hr.)
——— 0
.... 100
— — — 500

B— 2-Aminoanthraquinone
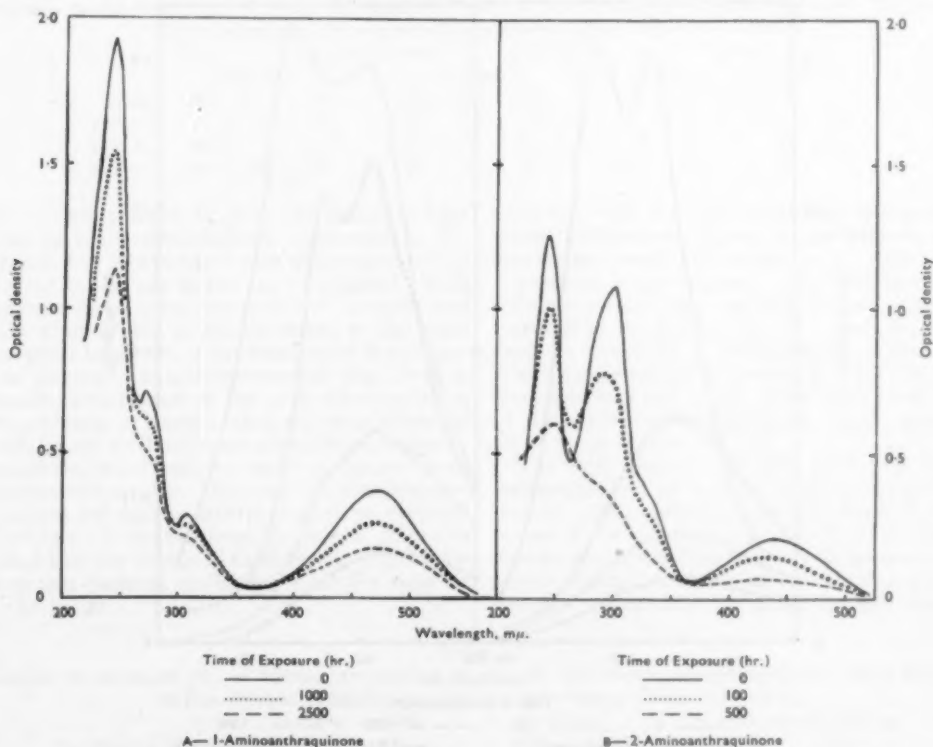
FIG. 1— Dyeings on Cellulose Acetate exposed in Dry Oxygen at 35°c. to High-pressure Mercury-vapour Lamp

acetate film about 1 mm. thick. Exposure was carried out in moist air, and the absorption spectrum was measured before and after irradiation. It is difficult to draw any conclusions from these results, since the absorption curve which these authors quote for the unexposed dyeing exhibits two bands in the visible region, although neither our own experiments [10] with this compound in solution or on transparent polymer films, nor those of Hartmann and Lorenz [13] for a solution in dioxan, are in agreement with this observation. On irradiation the dyed film of Moran and Stonehill darkens in intensity, and these authors have suggested that a "polymerised Aniline Black" may be formed. The suggestion has been made elsewhere [10] that Moran and Stonehill's sample of 1-aminoanthraquinone may not have been completely free from acid. If this suggestion is correct, the darkening effect may be the result of the action of light on the dyed film in the acid state.

The aminoanthraquinone compounds substituted in the 1 and 4 positions are characterised by twin absorption peaks in the visible region. On exposure to light in dry oxygen there is a decrease in these bands, which may be reduced in intensity with some preservation of band structure (Fig. 2), at any rate in the early stages of photochemical attack, or there may be a replacement of the twin-band system by a single absorption band as in Fig. 3. Changes of this kind are sometimes associated with a reddening of the dyed film. In

Time of Exposure (hr.)

——— 0
············ 1000
— — — 1500
— · — · 2500
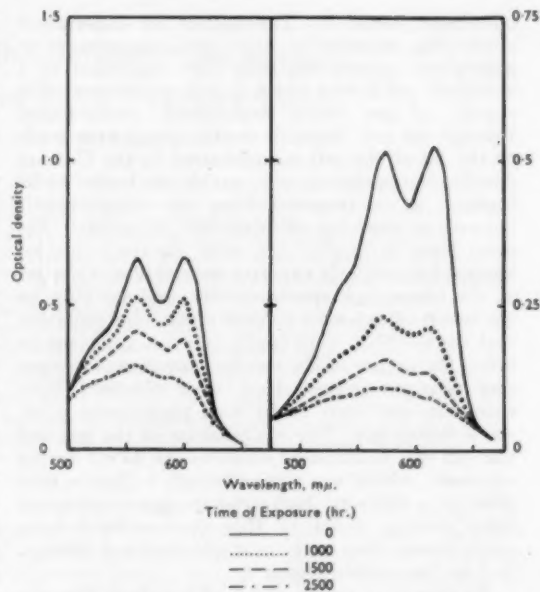
A— 1:4-Diaminoanthraquinone   B— 1:4:5-Triaminoanthraquinone

FIG. 2— Dyeings on Nylon exposed in Dry Oxygen at 35°c. to High-pressure Mercury-vapour Lamp

Time of Exposure (hr.)

——— 0   ············ 500   — — — 1000   — · — · 1500

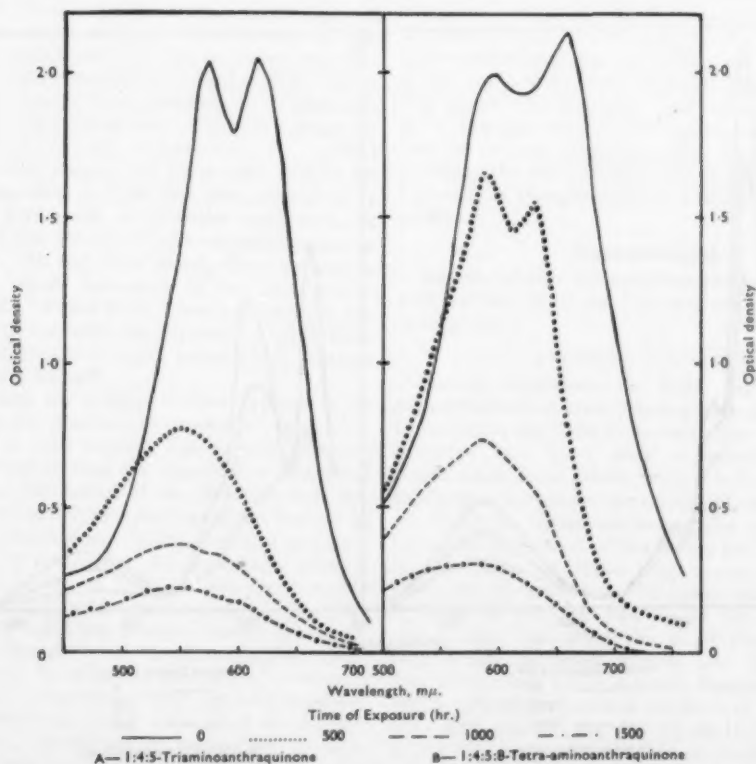A— 1:4:5-Triaminoanthraquinone   B— 1:4:5:8-Tetra-aminoanthraquinone

FIG. 3— Dyeings on N-Methoxymethylnylon exposed in Dry Oxygen at 35°c. to High-pressure Mercury-vapour Lamp

TABLE I

Decrease in Intensity (%) of Main Absorption Bands of 2-Aminoanthraquinone after Exposure in Dry Oxygen and Nitrogen to High-pressure Mercury-vapour Lamp

	Cellulose Acetate						Nylon			
	Nitrogen			Oxygen			Nitrogen		Oxygen	
λ, mμ.	243	300	433	243	300	433	302	462	302	462
100 hr. ...	29	44	50	19	28	33	28	41	35	39
300 hr. ...	44	64	70	37	54	57	41	57	64	66
500 hr. ...	46	68	78	52	67	66	52	61	79	82

Fig. 2 it is seen that, whilst the twin bands of 1:4-diamino- and 1:4:5-triamino-anthraquinone on nylon are initially reduced in intensity by comparable amounts, with increasing time of exposure the band at higher wavelengths is much more affected than is that at shorter wavelength.

With the 1:4:5-triamino compound on *N*-methoxymethylnylon the twin-band system at 575 and 616 mμ. is replaced after 500 hr. exposure by a general absorption band with a maximum at 550 mμ., although after this period of exposure the twin bands of the 1:4:5:8 compound on the same film are still observable. However, on further exposure of the latter amino compound these twin bands are replaced by a general absorption band at nearly the same wavelength as that of the lower of the twin peaks. In the early stages of photochemical attack it is again evident that the band at higher wavelength suffers proportionately greater reduction in intensity.

With 2-aminoanthraquinone the band at 243 mμ. seems to be less affected by light than the bands at 300 and 433 mμ., both in oxygen and in nitrogen. On the other hand, the fading of 1:5-diaminoanthraquinone on cellulose acetate film is appreciably faster in dry oxygen than it is in dry nitrogen (Table II). The general type of change in the absorption spectrum is similar in the two gases, however, in spite of the difference in the rate of fading. This is not so for the same dye on nylon. In both oxygen and nitrogen there are considerable decreases in the absorption in the visible band, but in the latter gas absorption increases on exposure in the region below 400 mμ., whereas in oxygen the reverse occurs. The change in the visible absorption band with the nylon dyeing is approximately the same in nitrogen and oxygen.

The order of light fastness of the various aminoanthraquinones upon the different substrate films differs from compound to compound as might be

TABLE II

Decrease in Intensity (%) of Main Absorption Bands of 1:5-Diaminoanthraquinone after Exposure in Dry Oxygen and Nitrogen to High-pressure Mercury-vapour Lamp

	Cellulose Acetate						Nylon			
	Nitrogen			Oxygen			Nitrogen		Oxygen	
λ, mμ.	230	277	487	230	277	487	280	497	280	497
100 hr. ...	4	2	3	18	13	30	0	29	25	26
300 hr. ...	20	17	17	56	56	51	−18	45	64	55
500 hr. ...	33	38	20	91	98	65	−45	55	95	70

It was not possible to study the action of light on all the aminoanthraquinone compounds in dry nitrogen, but it was found that substantial fading occurred in this gas in the cases examined. With 2-aminoanthraquinone on cellulose acetate and nylon films (Table I) the decreases in the main absorption bands are of the same order in nitrogen as in oxygen. On cellulose acetate film there is actually more change at the peak wavelengths in nitrogen than in oxygen when exposure times up to 300 hr. are used, although after 500 hr. exposure the differences between the results in the two gases are somewhat smaller. On nylon film the decreases in oxygen are slightly greater than those observed in nitrogen. It is clear from the results quoted in Table I that the change in the intensity of the main absorption peaks on irradiation is not the same for all the bands.

expected, but for any particular compound it seems that the least decrease in the intensity of the absorption bands, on exposure to light in an atmosphere of dry oxygen, occurs with dyeings on cellulose acetate film, an intermediate position is occupied by the dyeings on nylon, and the greatest decrease occurs on *N*-methoxymethylnylon. This is well illustrated by the results in Table III, which gives the decreases in the visible absorption bands of 1:4:5-triaminoanthraquinone dyed upon the three polymer films.

The light fastness of the individual aminoanthraquinones upon a given substrate seems to depend quite markedly upon the chemical constitution of the compound (Table IV). On cellulose acetate and nylon films the rates of decrease of the visible absorption bands of the 2-amino and 1:5-diamino compounds are much greater than are

TABLE III

Decrease in Intensity (%) of Visible Absorption Bands of 1:4:5-Triaminoanthraquinone after Exposure in Dry Oxygen to High-pressure Mercury-vapour Lamp for 1500 hr.

	Cellulose Acetate		Nylon		*N*-Methoxymethylnylon	
Wavelength, mμ. ...	560	600	575	615	575	615
Decrease, % ...	37	41	70	75	90	94

TABLE IV

Decrease in Intensity (%) of Visible Absorption Bands after Exposure in Dry Oxygen to High-pressure Mercury-vapour Lamp

Position of NH₂ Group(s)	Cellulose Acetate 500 hr.		Cellulose Acetate 2000 hr.		Nylon 500 hr.		Nylon 1000 hr.		N-Methoxy-methylnylon 500 hr.	
1	16		45		13		35		57	
2	66		ca. 100		82		ca. 100		83	
1:5	65		ca. 100		70		ca. 100		85	
1:4	11	14	40	46	9	10	20	22	32	48
1:4:5	16	14	47	50	29	34	56	62	65	81
1:4:5:8	15	16	45	52	21	28	48	65	20	59

those of the other aminoanthraquinones. With the three derivatives substituted in the 1 and 4 positions two figures are given in Table IV, which represent the values for the two visible bands (twin peaks), which characterise these compounds. The value on the left-hand side relates to the band of shorter wavelength. There is some evidence that the band at longer wavelength is slightly more affected by light than is the other component of the twin-band system. On the evidence available it is not easy to differentiate decisively between the light fastness properties of the 1-mono- and the three 1:4-di-substituted compounds. The rate of fading of all four compounds is of a comparable order on cellulose acetate film after both 500 hr. and 2000 hr. exposure. On the two nylon-type films the 1:4-diamino compound would seem to be the least affected by light, followed by the 1-amino compound.

The light stabilities of 2-aminoanthraquinone and the 1:5-diamino compound are clearly much less than those of the other four compounds. Under all conditions and upon all the films the 1-amino derivative is much more stable to light than the 2-amino compound, and similarly 1:4-diamino-anthraquinone is much less affected than is the 1:5 isomer.

The photochemical behaviour of some of the aminoanthraquinone compounds on N-methoxy-methylnylon film presents some interesting features. The results differ according to whether exposure is made in an atmosphere of nitrogen or oxygen. Thus, when 1-aminoanthraquinone is irradiated on this substrate in dry oxygen the main changes are a progressive decrease in the visible absorption band at 482 mμ. and on prolonged exposure an increase in absorption below 350 mμ., such that the small peaks at 275 and 312 mμ. are replaced by

FIG. 4— 1-Aminoanthraquinone dyed on N-Methoxymethylnylon exposed at 35°C. to High-pressure Mercury-vapour Lamp

Time of Exposure (hr.)

——— 0
········· 100
— — — 500

A— Dry Oxygen

Time of Exposure (hr.)

——— 0
········· 50
— — — 500

B— Dry Nitrogen

FIG. 5— 1:5-Diaminoanthraquinone dyed on *N*-Methoxymethylnylon exposed at 35°c. to High-pressure Mercury-vapour Lamp

Time of Exposure (hr.)

——— 0
········· 100
— — — 300

A— Dry Oxygen

Time of Exposure (hr.)

——— 0
········· 50
— — — 300

B— Dry Nitrogen
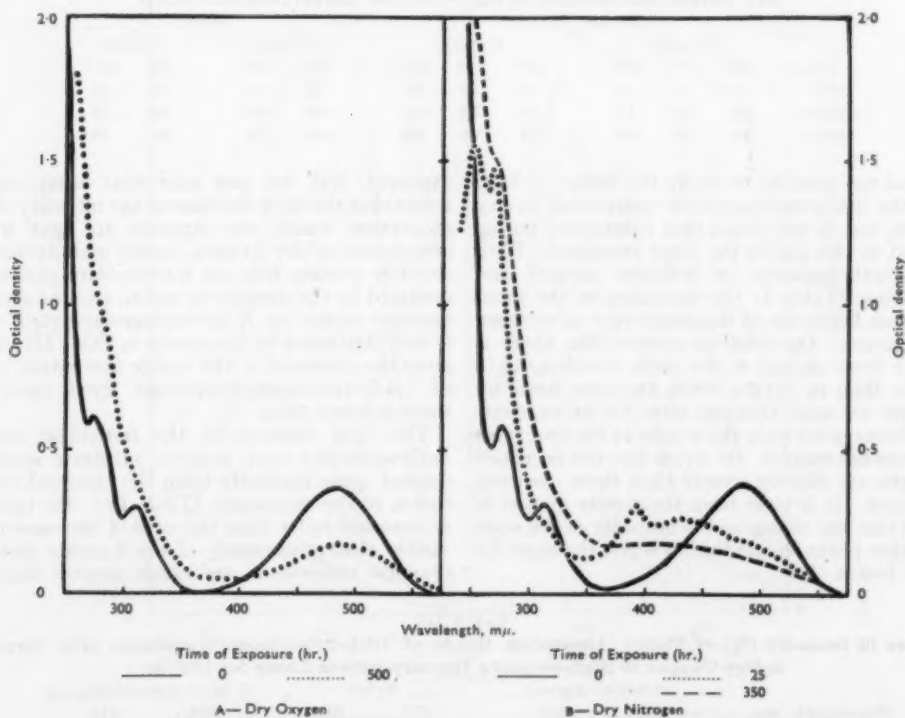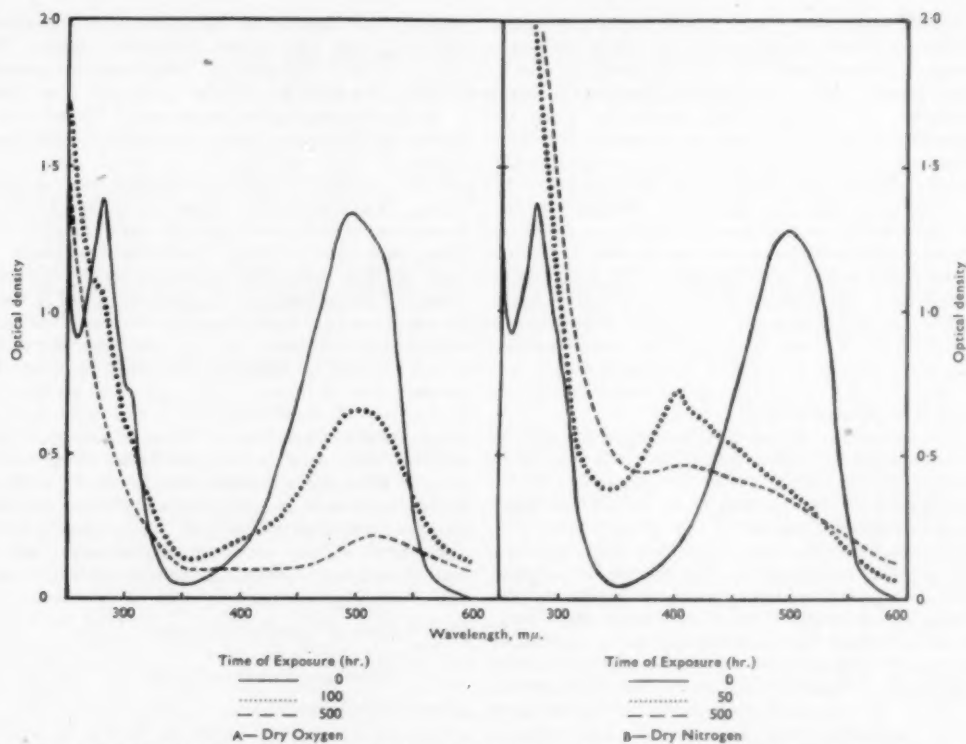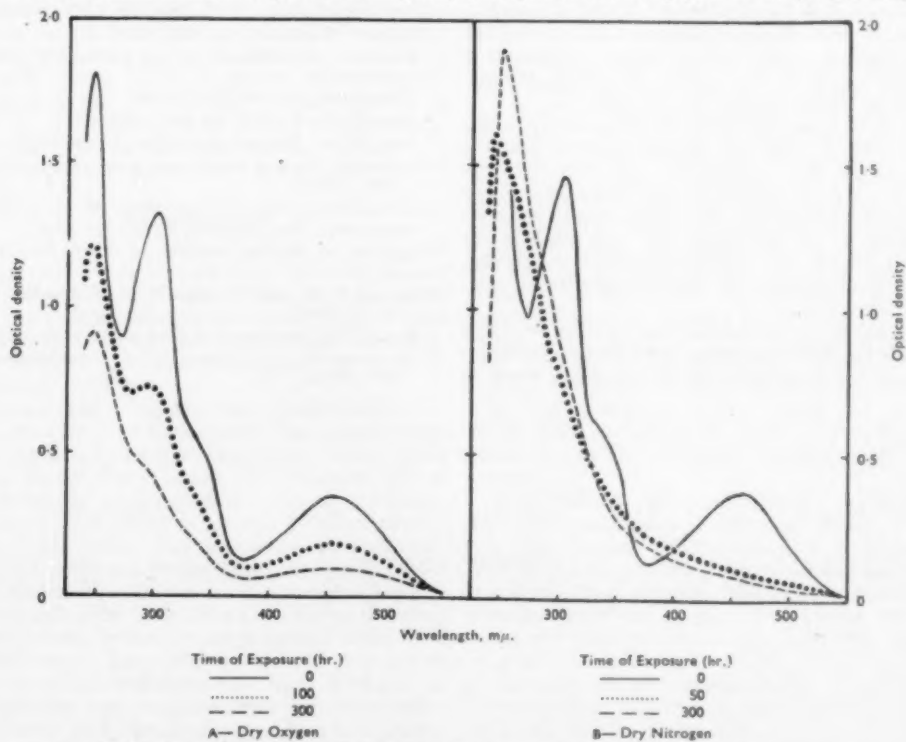
FIG. 6— 2-Aminoanthraquinone dyed on *N*-Methoxymethylnylon exposed at 35°c. to High-pressure Mercury-vapour Lamp

a general absorption band which has a maximum below the lowest wavelength at which measurements could be made (Fig. 4). In nitrogen, on the other hand, whilst the visible absorption band decreases on exposure and gradually loses its character, a new peak develops at about 390 mμ., which seems to increase in intensity as that in the visible region diminishes. Below 350 mμ. the small peak at 312 mμ. is largely eliminated, but the absorbance of the band at 275 mμ. becomes greater with little improvement in the definition of the band and a shift to about 270 mμ. There also seems to be evidence of the formation of a new peak at about 250 mμ. On prolonged exposure the new peak at 390 mμ. is reduced in intensity and ultimately eliminated, whilst the bands at 250 and 270 mμ. become submerged in a general absorption band of high intensity.

The behaviour of 1:5-diaminoanthraquinone on N-methoxymethylnylon film (Fig. 5) is somewhat similar to that of the 1-amino compound. In an atmosphere of dry oxygen there is not the same degree of intensification in the ultraviolet region as with the 1-amino compound, but there is still a considerable reduction in the visible absorption band. Exposure in dry nitrogen results in the formation of a new band at about 402·5 mμ., which increases in intensity up to a particular period of exposure, and then decreases on further irradiation. Below 350 mμ. the absorption increases on exposure to light in nitrogen much more markedly than in oxygen, but without revealing a new band in the short-wave ultraviolet region such as is found with the dyeing of 1-aminoanthraquinone. When exposures were carried out in dry oxygen, neither compound gave evidence of the formation of new peaks at about 400 mμ. similar to those observed in nitrogen.

The behaviour of 2-aminoanthraquinone seems to be markedly different from that of the 1-amino and 1:5-diamino compounds. In dry nitrogen (Fig. 6) there is a rapid and general decrease of the visible and ultraviolet absorption bands, with no indication of the formation of a new peak in the vicinity of 400 mμ. Fading is slower in oxygen, although ultimately the band structure is completely destroyed.

The photochemical behaviour of 1-amino- and 1:5-diamino-anthraquinone on N-methoxymethylnylon in an atmosphere of dry nitrogen must be regarded as anomalous in relation to the results obtained on the other substrate films. The explanation of this peculiar behaviour presumably lies in the nature of the polymer film itself. N-Methoxymethylnylon is produced by reaction of nylon (polyhexamethylene-adipamide) with formaldehyde and methanol, so that the group $>$N·CH$_2$·O·CH$_3$ is introduced into the polymer chain. It is known that, under suitable conditions, formaldehyde can be split off compounds of this kind, and also off urea–formaldehyde resins. It may be that under the action of light very small traces of formaldehyde are liberated, and it would be expected that these traces would react with the aminoanthraquinone, but it is not clear why such a change should be readily observed in nitrogen, but no evidence be found in oxygen. It is known that a number of dyes exhibit a lower light fastness than usual on cellulosic fabrics which have been treated with a urea–formaldehyde resin, and it may be that there is some connection between the fading of dyes on N-methoxymethylnylon and such textile materials. Further work, however, is necessary before such a connection can be established, and before the nature of the changes on N-methoxymethylnylon can be elucidated.

DEPARTMENT OF TEXTILE CHEMISTRY
    FACULTY OF TECHNOLOGY
        UNIVERSITY OF MANCHESTER

References

[1] Cunliffe, P. W., J. Textile Inst., 15, T 173 (1924).
[2] Hibbert, E., J.S.D.C., 43, 292 (1927).
[3] Scholefield, F., Hibbert, E., and Patel, C. K., ibid., 44, 236 (1928).
[4] Hibbert, E., ibid., 45, 204 (1929).
[5] Blaisdell, B. E., ibid., 65, 618 (1949).
[6] Bolis, M. A., Rev. gén. Mat. color., 12, 289 (1908).
[7] Scharwin, W., and Pakschwer, A., Z. angew. Chem., 40, 1008 (1927).
[8] Ackermann, J. W., J. Phys. Chem., 36, 780 (1932).
[9] Couper, M., Text. Research J., 21, 720 (1951).
[10] Egerton, G. S., and Roach, A. G., J.S.D.C., 74, 401 (1958).
[11] Barnes, B. T., and Forsythe, W. E., J. Opt. Soc. Amer., 27, 83 (1937).
[12] Moran, J. J., and Stonehill, H. I., J.C.S., 779 (1957).
[13] Hartmann, H., and Lorenz, E., Z. Naturforschung, 72, 360 (1952).

Studies on Aminoanthraquinone Compounds
III— Photochemistry in the Solid State

G. S. EGERTON and A. G. ROACH

Solid transparent films on quartz of six aminoanthraquinone compounds (1-mono-, 2-mono-, 1:4- and 1:5-di-, 1:4:5-tri-, and 1:4:5:8-tetra-aminoanthraquinone) have been prepared by vacuum deposition. The action of (a) near ultraviolet radiation and visible light and (b) short-wave ultraviolet radiation (mainly 253·7 mμ.) on these solid films has been studied spectrophotometrically. The stability of the solid dye to (a) is shown to be substantially greater than when the dye is present in the form of a dyeing on a polymer film. In moist air the photochemical stability of the solid dye is much less than in dry oxygen or dry nitrogen. The nature of the changes occurring as a result of irradiation in these atmospheres is also different, and reasons for these differences are discussed. The action of (b) on the solid dye is shown to lead to rapid destruction of the dye. The rate is greater in dry oxygen than in dry nitrogen, and ultimately all the dye and photoproducts appear to be removed from the quartz. 2-Aminoanthraquinone is most rapidly affected by (a) but is the most stable of the six compounds to (b).

Introduction

It has been shown [1, 2] that level transparent dye films can be produced by vacuum deposition of purified aminoanthraquinones. Since the dye is present in this case upon an inert substrate, quartz, it seemed of interest to compare the changes which might occur on irradiation of these films of solid dye with results which have been obtained [3] with the aminoanthraquinones dispersed as dyeings in polymer films. The photochemical stability of a dye is known to depend upon the substrate upon which it is present, and presumably the particle size of the dye and its bonding to the polymer molecules are among the factors involved in these differences in photochemical behaviour. In the absence of the polymer the latter factor is eliminated, although it seems possible that it is replaced by another factor, the bonding of the dye molecules with one another. In the study of the action of short-wave ultraviolet radiation on the dye, the use of solid deposits on quartz is preferable to that of dyed polymer films, since this type of radiation has a profound and complicated effect upon the polymer itself [4-6].

Experimental

Many of the experimental details have already been given [2, 3]. A low-pressure mercury-vapour lamp (Thermal Syndicate Ltd.), shaped in the form of a U-tube and operated vertically, was used as the source of short-wave ultraviolet radiation. Over 96% of the radiation from this lamp is emitted at 253·7 mμ.

Films of solid dye on small pieces (35 mm. × 7 mm. × 1 mm.) cut from quartz microscope slides were prepared by vacuum deposition. These small quartz plates fitted inside the standard quartz cells in which exposures were made in dry gases. The plates were firmly supported by silver frames inside these cells. For exposures in moisture-saturated air to the Osram lamp the quartz plates fixed in the silver frames were supported inside a large closed glass cell (15 cm. × 15 cm. × 2·5 cm.) at the bottom of which was a trough filled with distilled water. The silver frames with the quartz plates were removed from this large glass cell as required for spectrophotometric measurements, which were made inside an open standard quartz cell against a clean quartz plate in a similar cell.

All quartz plates and cells were rigorously cleaned before use.

The most significant factors affecting the production of level and transparent dye films by vacuum deposition appear to be the cleanliness of the quartz plate and the deposition chamber, the purity of the compound used, the accurate alignment in a horizontal plane of the quartz plate above the sample of dye, and the rate at which the build-up of compound on the plate occurs during deposition. No change in the spectrum of the solid film on quartz was observed when the dry gas was passed through the cell while the film was kept in the dark for 2500 hr.

Discussion of Results

ACTION OF NEAR ULTRAVIOLET RADIATION AND VISIBLE LIGHT

The visible absorption spectrum of indigo in the solid phase and in solutions in organic solvents was determined some years ago by Sheppard and Newsome [7]. These workers found that the absorption band was present at considerably longer wavelengths in the solid phase. More recently this large shift in the absorption band of indigo has been studied by Weinstein and Wyman [8], who have pointed out that this phenomenon is characteristic of indigoid dyes which do not carry bulky substituents in the 4 and 7 positions. They have suggested that in the solid phase indigo is present in the form of dimers or higher polymers, which are held together by intermolecular hydrogen bonds linking the carbonyl group of one indigo molecule with the secondary amino group of another. Bulky substituents in the 4 and 7 positions will make it difficult for these hydrogen bonds to be formed.

This postulate also seems to be applicable to aminoanthraquinones in the solid phase, since it has been shown [2] that there is a bathochromic shift of the near ultraviolet and visible absorption bands of 1- and 2-amino- and 1:5-diamino-anthraquinone when the spectra in the solid state are compared with the results obtained with solutions in *n*-hexane and ethyl alcohol. For these three compounds the wavelength shifts relative to the corresponding solutions in ethyl alcohol amount to 8 and 15 mμ., 2 and 3 mμ., and 9 and 14 mμ. respectively. The first value relates to the near

ultraviolet band and the other to the visible band. It will be noted that the band wavelengths of the 2-amino compound are less affected on change from the solution to the solid state. On the basis of the reasoning which Weinstein and Wyman [8] have used it would therefore seem possible that in the solid films on quartz complexes of the type I might be formed. There is also the possibility that with di-substituted derivatives intramolecular bonds are formed, so that complexes similar to type II may be present in the solid phase. With 2-amino-anthraquinone stereochemical considerations make it seem likely that only one hydrogen bond will be formed between two molecules. The smallness of the bathochromic shift with this compound seems to support this idea.

(I)　　　　　　(II)
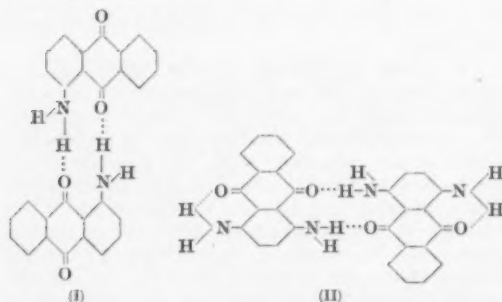
In solution 1:4-diaminoanthraquinones show twin peaks in the visible region which are replaced by a general absorption band in the solid state [2]. Allen, Wilson, and Frame [9] have suggested that the ionic form III is responsible for the appearance of the twin peaks. The formation of dimers or higher polymers similar to I or II when the compound is in the solid phase would mean that reversion to the ionic form was no longer possible and the twin peaks would be suppressed. The photochemical stability of these associated molecules would be expected to be substantially greater than that of the simple parent molecules, and this seems to be borne out in practice when the action of near ultraviolet radiation and visible light on solid films of these compounds on quartz is studied.

(III)
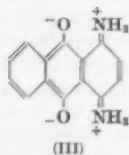
Thus, if the data given in Table I, for the decrease in intensity of the visible absorption band of the compound in the solid state after exposure in dry oxygen to a 400-w. Osram high-pressure mercury-vapour lamp, are compared with the corresponding values for dyeings on films of cellulose acetate and nylon [10], the marked photo-chemical stability of the dye in the solid state is obvious. Only with 2-aminoanthraquinone is the compound in the solid state substantially affected after 2000 hr. exposure. The concept of inter-molecular bonding, which for stereochemical

reasons cannot be fully applied to this compound, unlike the other aminoanthraquinones studied, would seem to be in agreement with these results. The superior stability of the 1:4-derivatives when the twin peaks are suppressed is particularly noticeable.

TABLE I

Solid Films on Quartz exposed in Dry Oxygen to High-pressure Mercury-vapour Lamp

Position of NH₂ Groups	Exposure (hr.)	Decrease in Intensity of Visible Absorption Band (%)
1	2500	14
2	2000	43
1:5	2000	15
1:4	2500	0
1:4:5	2500	6

It has been observed [3] that when dyeings on cellulose acetate or nylon films are exposed to light in dry nitrogen considerable fading of the dye may occur. The extent of fading seems to depend, however, upon the substrate film and upon the particular aminoanthraquinone. Presumably one of the controlling factors is the bond, if any, between the compound and the substrate. The fact that fading occurs with both 2-mono- and 1:5-di-aminoanthraquinone must mean that there is some photochemical reaction in which the polymer film is involved. With the solid film of these dyes on quartz reaction with the inert base is improbable, and any change which occurs on irradiation in dry nitrogen must presumably involve an internal rearrangement of the dimer (or higher polymer) or the reaction of one dye molecule with another in a disproportionation reaction.

The changes which occur when a solid film of 2-aminoanthraquinone is irradiated in dry nitrogen and dry oxygen are illustrated in Fig. 1. In the latter gas the photochemical attack on the amino-anthraquinone leads to a reduction in intensity at all wavelengths throughout the spectrum, and presumably this is due to oxidation of the dye. This type of reaction is not directly possible in an atmosphere of dry nitrogen, and here any change of this kind must involve disproportionation. As evidence that this may occur, it will be noted that, while some weakening of the visible and near ultraviolet absorption bands occurs, there is an intensification of the absorption below 275 mμ., suggesting the development of unsaturated centres. This type of behaviour is, perhaps, more marked with 1:5-diaminoanthraquinone (Fig. 2), where in dry nitrogen irradiation produces a marked intensification of the absorption in the ultraviolet region with little change in the visible band. In dry oxygen, on the other hand, there is a noticeable decrease in the intensity of the near ultraviolet and visible bands.

The formation of intermolecular hydrogen bonds between molecules of aminoanthraquinones in the solid state would probably be affected by the presence of water or water vapour. It could therefore be expected that the photochemical stability of these compounds would be less in

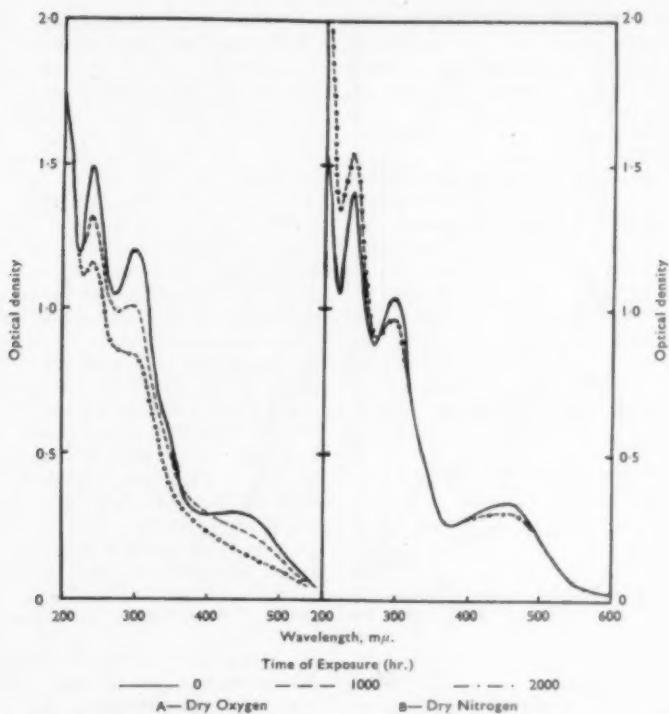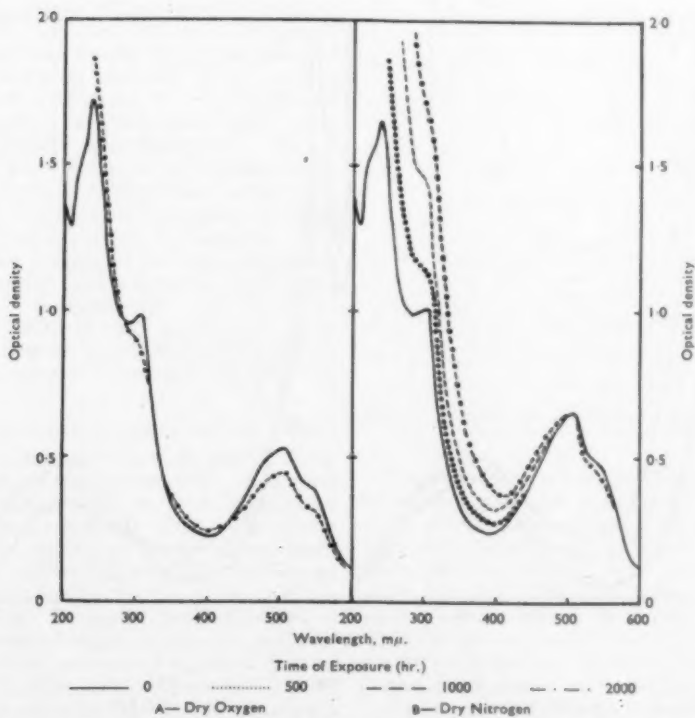FIG. 1— 2-Aminoanthraquinone on Quartz exposed at 35°C. to High-pressure Mercury-vapour Lamp

FIG. 2— 1:5-Diaminoanthraquinone on Quartz exposed at 35°C. to High-pressure Mercury-vapour Lamp
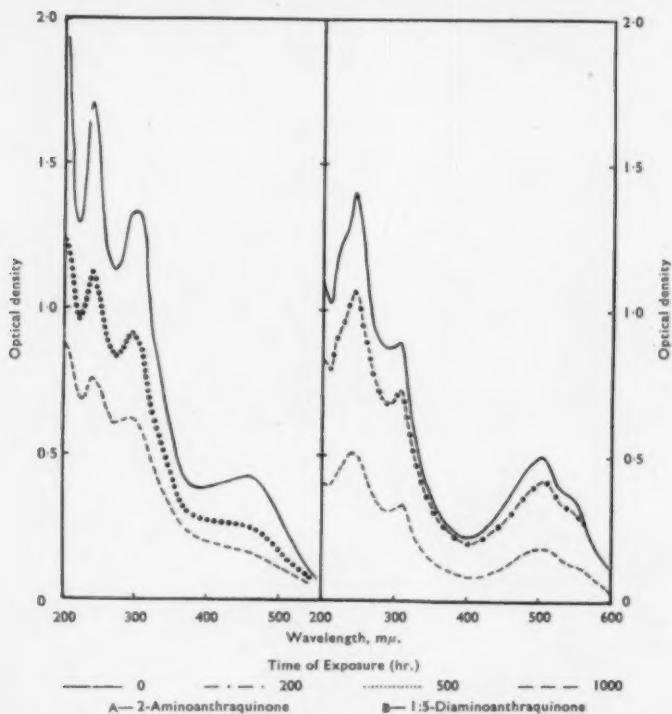
FIG. 3— Dye Films on Quartz exposed in Moisture-saturated Air at 35°C. to High-pressure Mercury-vapour Lamp
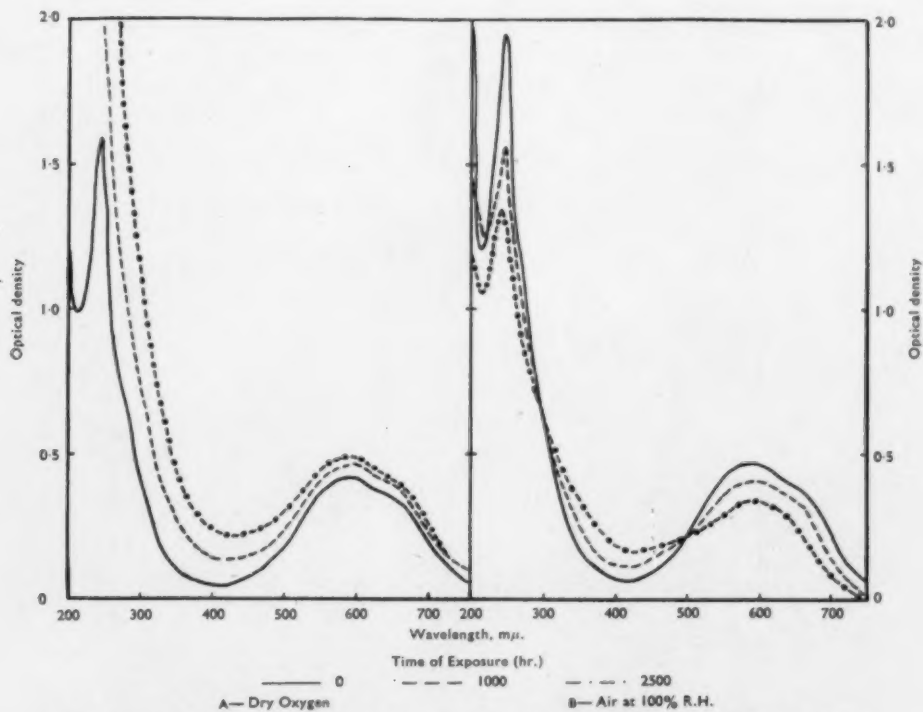
FIG. 4— 1:4:5:8-Tetra-aminoanthraquinone on Quartz exposed at 35°C. to High-pressure Mercury-vapour Lamp

moist atmospheres. The curves in Fig. 3 for the solid films of 2-aminoanthraquinone and 1:5-diaminoanthraquinone show that on irradiation in an atmosphere saturated with water vapour the loss in intensity of the absorption bands is very much greater than when exposure is made in dry oxygen. With 2-aminoanthraquinone the fading in the latter gas (Fig. 1) seems to be somewhat similar in characteristics to that in moist air, although considerably slower in its occurrence, but the behaviour of 1:5-diaminoanthraquinone seems to be different in the two gases. Apart from the large difference in the rate of fading, the high-intensity band at 242 mμ. seems to be progressively reduced in intensity on irradiation in moist air but intensified in dry oxygen. The behaviour of 1-aminoanthraquinone is very similar in this respect to that of the 1:5-diamino compound. Some of the differences between the results in the dry and moist atmospheres may be the result of the formation of hydrogen peroxide, which is known to occur when anthraquinonoid vat dyes are exposed to light in the presence of air and water vapour [11]. The action of the peroxide vapour on the aminoanthraquinone might involve reaction of the latter with OH or HO$_2$ radicals produced from the peroxide and would undoubtedly be complex in nature.

With 1:4-diaminoanthraquinone there is no change on irradiation of the solid film in dry oxygen for 2500 hr., but in moist air after the same period of exposure there is a significant drop in the intensity of the ultraviolet and visible absorption bands. The behaviour of solid films of 1:4:5-tri- and 1:4:5:8-tetra-aminoanthraquinone is perhaps more reminiscent of that of the 1:5-diamino compound in that the results in dry oxygen and moist air are different in character. In dry oxygen there seems to be a tendency for the ultraviolet bands to intensify on irradiation, whereas in moist air the bands are weakened. This is illustrated in Fig. 4 for 1:4:5:8-tetra-aminoanthraquinone. Both ultraviolet and visible bands of this compound are reduced in intensity in moist air, but the reverse occurs in dry oxygen. With the 1:4:5-triamino compound there is a slight fall in the intensity of the visible band but a relatively greater increase in the intensity of the ultraviolet band after irradiation in dry oxygen. In moist air the changes appear to be smaller than in dry oxygen, with quite small decreases in the intensity of both bands.

ACTION OF SHORT-WAVE ULTRAVIOLET RADIATION

Study of the changes produced in aminoanthraquinone compounds by short-wave ultraviolet radiation is a complicated problem when these dyes are present on polymer films. The short-wave radiation is capable of producing profound changes in the undyed polymer film, which are almost certainly initially due to photolytic decomposition of the polymeric molecules. As a result of the restricted freedom inside the polymer mass, free radicals of relatively long life appear to be formed [4-6]. Experimentally these changes are manifest in a considerable rise in the ultraviolet absorption of the polymer film on irradiation, with

a tendency for the absorption to increase further on storage in the dark. Another complicating factor is that on further irradiation after storage in the dark the optical density of the film initially drops and then starts to rise again. An accurate assessment of the changes produced in a dyed polymer film irradiated with short-wave ultraviolet radiation would obviously present difficulties if only the absorption spectrum of the dyed film was measured. Any measurements against the corresponding undyed film would involve the assumption that the free radicals formed from the polymer did not have a significant effect upon the rate of fading. The solid dye films on quartz have the advantage that the substrate is relatively inert and free from changes of the above nature. Nevertheless, it is likely that free radicals are again formed, but in this case from the molecules of the dye.

Time of Exposure (hr.)

——— 0
— — — 25
— · — · 50
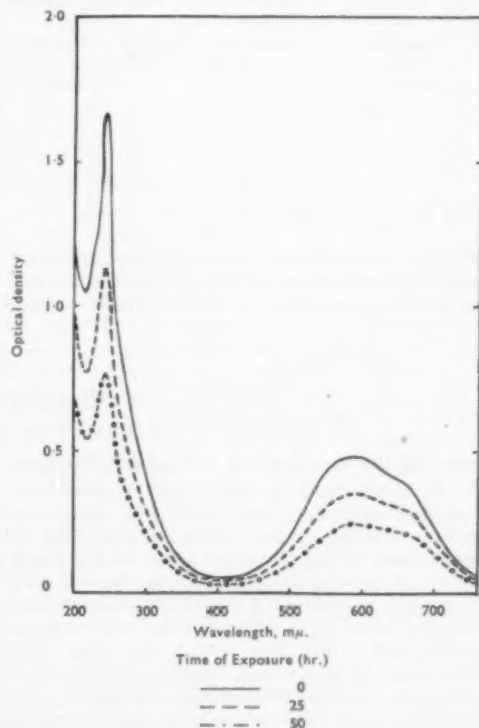
FIG. 5— 1:4:5:8-Tetra-aminoanthraquinone on Quartz in Dry Oxygen at 35°C. exposed to a Low-pressure Mercury-vapour Lamp

The characteristic feature of the results obtained by exposing the solid dye films on quartz to short-wave ultraviolet radiation is a general uniform decrease in absorption throughout the spectrum, as illustrated in Fig. 5 for 1:4:5:8-tetra-aminoanthraquinone. The photolytic decomposition is similar in character in both dry oxygen and dry nitrogen, but is considerably more rapid in the former atmosphere. With all six aminoanthraquinones there is a rather surprising consistency in the way the bands at all wavelengths decrease in intensity at the same rate. This type of behaviour

occurs also when the solid dye films are exposed in moist air to the Osram lamp, but not when exposures are made in dry gases. The uniform decrease at all wavelengths would seem to imply removal from the system of the photochemical products of decomposition or, what is less likely, the production of fully saturated non-absorbing compounds. After a considerable exposure period (about 750 hr.) in dry oxygen to the low-pressure mercury-vapour lamp the quartz plates, which originally supported dye films, possessed absorption characteristics similar to those observed for the standard quartz plates after cleaning and before use in deposition experiments. Thus it would appear that the photoproducts are ultimately almost completely removed from the exposed surfaces.

TABLE II

Solid Films on Quartz exposed in Dry Oxygen and in Dry Nitrogen to Low-pressure Mercury-vapour Lamp for 50 hr.

Position of NH_2 Groups	Decrease in Intensity of Visible Absorption Band (%)	
	Oxygen	Nitrogen
1	67	40
2	38	8
1:5	66	20
1:4	63	17
1:4:5	73	21
1:4:5:8	47	12

The rate at which the aminoanthraquinones are affected by short-wave ultraviolet radiation differs from the corresponding rate for exposure to near ultraviolet radiation and visible light. The most stable of the six compounds is apparently 2-amino-anthraquinone (Table II), although this is the least stable to near ultraviolet radiation and visible light. The stability of the 1:4-diamino compound, which is a marked feature where the latter type of radiation is concerned, is now rather poor. These differences in stability would seem to be related to the formation of intermolecular complexes, but a satisfactory explanation of the reason why these complexes are more affected than the parent molecules by short-wave ultraviolet radiation will require further study. The photolytic decomposition of the dye is, however, clearly much more rapid in the presence of oxygen, although it is not prevented by absence of the latter.

DEPARTMENT OF TEXTILE CHEMISTRY
FACULTY OF TECHNOLOGY
UNIVERSITY OF MANCHESTER

References

[1] Egerton, G. S., and Roach, A. G., Nature, 179, 491 (1957).
[2] Idem, J.S.D.C., 74, 401 (1958).
[3] Idem, ibid., 74, 408 (1958).
[4] Idem, Nature, 180, 189 (1957).
[5] Egerton, G. S., and Fitton, S. L., ibid., 178, 41 (1956).
[6] Ford, R. A., ibid., 176, 1023 (1955).
[7] Sheppard, S. E., and Newsome, P. T., J. Amer. Chem. Soc., 64, 2937 (1942).
[8] Weinstein, J., and Wyman, G. M., ibid., 78, 2387 (1956).
[9] Allen, C. F. H., Wilson, C. V., and Frame, G. F., J. Org. Chem., 7, 169 (1942).
[10] Egerton, G. S., and Roach, A. G., J.S.D.C., 74, 412 (Table IV) (1958).
[11] Egerton, G. S., ibid., 65, 764 (1949).

CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

Errors in the Assessment of Colour Fastness

G. G. Bradshaw[1] is quite right to challenge Bülow and Horrdin's assertion[2] that their conclusions concerning the variations occurring in light-fastness testing should be valid for the I.S.O. method. Reporting light fastness on the 1–8 scale undoubtedly suggests that the exposures have been assessed against light-fastness standards exposed simultaneously, but this is not the case. The method used by Bülow and Horrdin is that part of the Swedish Standard SIS 650013 (dated September 1950) which deals with fading-lamp exposures, and briefly this consists in determining if an obvious change (*tydling ändring*) is produced on the specimen in $2\frac{1}{2}$, 5, 10, 20, 40, 80, or 160 hr.; if it occurs in $2\frac{1}{2}$ hr. or less, the light fastness is said to be 1, in 5 hr. 2, etc. This critical value is thus subjective and therefore vague, and it is not surprising that these authors found the observer factor to be the largest component of the total variance. It is interesting to note that the originators of this test, the AATCC, no longer rely on a subjective description of the critical value: they define it as "the degree of contrast . . . which is visually equal to step 4 of the International Gray Scales for assessing the effect on the pattern in fastness testing" (Standard Test Method 16A–56).

The explanation given in the subsequent letter[3] is not, therefore, valid: in the I.S.O. method, the assessor does not have ". . . to decide whether the difference in colour of the fabric has reached a certain critical value" or not: he has to expose the specimen so as to produce two or three different degrees of colour contrast and to decide which of the eight standards exposed simultaneously and in identical manner is nearest to the specimen in so far as overall visual contrast is concerned. At each degree of specimen contrast, therefore, one has for comparison standards showing various degrees of contrast ranging from smaller, through approximate equivalence, to greater, the change in contrast increasing regularly. This will undoubtedly reduce both the time factor and the observer factor, and these two account for 70% of the total variance found.

Bülow and Horrdin have not, therefore, provided a convincing reason for believing that their conclusions, although probably beyond reproach as far as testing by the old American method is concerned, are also of equal validity for the I.S.O. method. Until a similar investigation conclusively proves that the accuracy of the I.S.O. method is poor, my experience of over 200,000 light-fastness assessments made during

the past eight years leads me to agree unreservedly with G. G. Bradshaw when he says: "it is very difficult to believe that assessment made by the present I.S.O. method of daylight exposures and with trained observers is of such doubtful accuracy."

K. McLAREN

DYEHOUSE DEPARTMENT
   IMPERIAL CHEMICAL INDUSTRIES LTD.
      DYESTUFFS DIVISION
         P.O. BOX 42
           HEXAGON HOUSE
             MANCHESTER 9

6th March 1958

McLaren is quite right that the blue standards 1–8 were not used in our investigation, but in the I.S.O. method, as well as in SIS 650013, there are certain sources of variation in the visual assessment of the specimens. Regarding the I.S.O. method §§ 5 and 7.5.1, these are—

(1) Specimen and standards should be exposed in such a manner that one contrast equal to Grade 4 on the grey scale and one contrast equal to Grade 3 are obtained on the specimen. It will always be a subjective matter to decide when these contrasts or critical values have been reached.

(2) When contrasts equal to Grades 4 and 3 have been established on the specimen, a decision must be made which of the blue standards show identical contrasts. This operation does not differ essentially from assessing change in colour with the grey scale: there are only a number of faded blue standards instead of the grey scale, and it will undoubtedly include an important subjective component.

(3) It might happen, and this is in our experience not infrequently the case, that different fastness ratings are obtained at the two different degrees of contrast. The I.S.O. Subcommittee has obviously noted this disadvantage, and has recently published a supplement [4]—

> If two different assessments are obtained at the two different degrees of contrast, the light fastness of the specimen is the arithmetic mean of these two assessments.

By such a procedure this part of the assessment variation is reduced, but not eliminated.

Considering these sources of assessment variation, we feel convinced that there is a considerable uncertainty in the I.S.O. method as well as in SIS 650013, simply because both deal with subjective estimates of colour contrasts. McLaren seems to attach less importance to the assessment variation than we do, but in an investigation in 1952 he found [5] by means of the grey scale and probably trained observers a variation in assessment of the same magnitude as the one we have found for the SIS method. The patterns showed mainly changes in hue, but this fact is not very important in this case.

We agree with McLaren that an investigation of the errors of the I.S.O. method should be of great value in removing any doubt about the accuracy of this method.

ULF BÜLOW
STURE HORRDIN

BORÅS WÄFVERI AB.
   BORÅS
      SWEDEN
17th March 1958

[1] Bradshaw, G. G., J.S.D.C., **74**, 88 (Feb. 1958).
[2] Bülow, U., and Horrdin, S., *ibid.*, **73**, 459 (1957).
[3] Idem, *ibid.*, **74**, 89 (Feb. 1958).
[4] *Ibid.*, **74**, 25 (Jan. 1958).
[5] McLaren, K., *ibid.*, **68**, 205 (1952).

Behaviour of Reactive Dyes on Wool

Although the recently introduced reactive dyes (Procions and Cibacrons) are intended for application to cellulosic fibres, it has been indicated that in certain instances they may be of use in wool dyeing [1].

When applied to cellulosic fibres under certain conditions, the Procion dyes are stated to give stable cross-links, which render the dyed fibre insoluble in a solution of cuprammonium hydroxide [2]. It was therefore of interest to study their reaction with wool, and the changes produced have been measured by means of the urea–bisulphite solubility method [3].

Preliminary experiments showed that the effect of reactive dyes might be more easily seen by using chlorinated wool, and a series of three Procion (ICI) and three Cibacron (Ciba) dyes were applied to chlorinated and unchlorinated yarn according to the suggested method for wool [1]. Dyeings were made from a bath containing 1% formic acid, and the dyed yarn was aftertreated in a bath containing 2% ammonia at 40°c. for 15 min. Before dyeing, the yarn was wet-chlorinated by the standard method [4] with 1 g. available chlorine per litre.

The results are given in the following table, from which it may be seen that with the Procion dyes there is an appreciable fall in the urea–bisulphite solubility of the dyed yarn. With the three Cibacron dyes used no such changes were observed.

Urea–Bisulphite Solubility (%)

	Unchlorinated Yarn	Chlorinated Yarn
Blank dyeing	36·3	53·4
10% Procion Yellow RS	13·4	11·5
10% Procion Brilliant Red 2BS	27·4	26·8
10% Procion Blue 3GS ...	23·1	23·5
10% Cibacron Yellow R ...	39·4	49·3
10% Cibacron Brilliant Red 3B	38·6	56·9
10% Cibacron Blue 3G ...	39·0	53·7

As Procion Yellow RS gave the greatest change in urea–bisulphite solubility, this dye was used to study the effect of concentration on unchlorinated yarn. The results are given in the following graph in comparison with the behaviour of Kiton Fast Yellow 2GL (C.I. Acid Yellow 17). This dye was also applied from a bath containing 1% formic acid, but no aftertreatment with ammonia was given. With both dyes, blank dyeings were made under the appropriate conditions to take account of any differences in urea–bisulphite solubility

resulting from differences in the two dyeing methods used.

Dye applied, %

—○— Procion Yellow RS
--●-- Kiton Fast Yellow 2GL
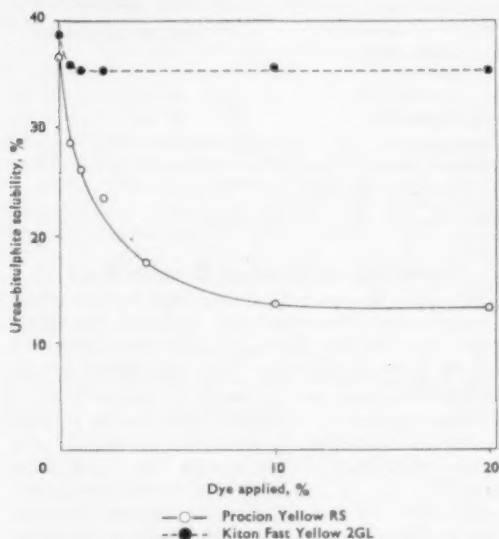
The urea–bisulphite solubility of wool can be reduced by the action of alkali [3], which forms stable cross-linkages, and the present results indicate that the three Procion dyes are capable of forming stable cross-linkages within the wool fibre. The three Cibacron dyes, however, do not appear to form such cross-linkages, and this may indicate either that these dyes contain only one reactive group, or that, if more than one reactive group is present, the position of such groups does not allow cross-linking to take place.

F. MANCHESTER

WOOL INDUSTRIES RESEARCH ASSOCIATION
  TORRIDON
    LEEDS 6

17th March 1958

[1] ICI, *Procion Dyestuffs in Textile Dyeing* (1956), p. 18.
[2] Vickerstaff, T., J.S.D.C., **73**, 237 (1957).
[3] Lees, K., and Elsworth, F. F., *Proc. International Wool Textile Research Conf. Australia*, **C**, 363 (1955).
[4] Society of Dyers and Colourists, *Standard Methods for the Assessment of the Colour Fastness of Textiles* (Bradford, 1955), p. 22.

Potential Alkalinity of Dyehouse Water

The passing reference to the potential alkalinity of dyehouse water in the recent paper by Richardson [1] is worthy of amplification.

When water containing temporary hardness is softened by the base-exchange process, calcium and magnesium bicarbonates are converted into an equivalent amount of sodium bicarbonate, which is then converted to the normal carbonate with accompanying high alkalinity, even after a normal dyehouse atmospheric "boil".

The carbonate–bicarbonate composition of a dyehouse water may be almost completely reversed after only 30 min. boiling—

	Before Boiling	After Boiling for 30 min., cooled to 20°c.
Carbonates	4 p.p.m.	122 p.p.m.
Bicarbonates	121 p.p.m.	3 p.p.m.
pH	7·5	10·5

The large pH change which occurs as the temperature rises is most detrimental to the application of molecularly aggregated acid, metachrome, 1 : 2 metal-complex, and some chrome dyes to wool.

Increase in alkalinity at elevated temperatures completes the conditions required for (*a*) severe attack on the wool fibre by producing accelerated disulphide-bond fission (hydrogen sulphide may be detected in the water vapour escaping from the boiling dye liquor) and (*b*) retarded dye exhaustion, necessitating the addition of acid under the worst conditions for the production of level dyeings.

The presence of ammonium sulphate has little effect in promoting exhaustion, and on extended boiling tends to assist in maintaining only slightly less alkaline conditions. For waters of high bicarbonate content, therefore, ammonium sulphate may be omitted and replaced with free acid. This is particularly required when dyeing above 100°c.

By pretreating the wool at 50°c. for 15 min. in acid solution, usually acetic acid, to lower the starting pH sufficiently (*a*) to correct the alkalinity from scouring (thereby removing possible pH gradients throughout the wool), (*b*) to avoid the potential alkalinity of the water, and (*c*) to promote economic exhaustion, the rate of exhaustion may be controlled by a controlled rate of rise in temperature, usually 1°c. per minute.

Bicarbonate water permits a further modification in metachrome dyeing: the more acidic dichromate may be substituted for the neutral chromate or metachrome mordant, and dyeing may be carried out in a dichromate–acetic acid liquor. Ammonium sulphate is then omitted.

J. WALTON

7 CRESTA GARDENS
  MAPPERLEY RISE
    NOTTINGHAM

28th February 1958

Production of high alkalinities from zeolite-softened bicarbonate waters is well known. The effect of such waters on the dyeing of cellulosic fibres in particular has been dealt with adequately in the *Journal* [2, 3]. The problem can be serious enough, however, and is so often overlooked as to make emphasis of this point worthwhile. For example, additions of acid—as may be recommended in technical literature—always need modifying to take care of the alkalinity present in the water supply.

R. W. RICHARDSON

COURTAULDS LTD.
  COVENTRY

19th March 1958

[1] Richardson, R. W., J.S.D.C., **73**, 485 (1957).
[2] Ashpole, D. K., McFarlane, R. A., and Wilcock, C. C., *ibid.*, **66**, 17 (1950).
[3] Armfield, W., *ibid.*, **67**, 297 (1951).

Notes

Meetings of Council and Committees
April
Council— 2nd

Publications Committee— 15th

Examinations Board— 3rd

International Federation 1959 Congress— Social Subcommittee— 29th

Data on Identification of Dyes on Textile Fibres— 18th

Light Fastness Subcommittee— 17th

Subcommittee on Refereeing— 15th

Annual General Meeting— 25th

Annual Meeting of Chairmen and Honorary Secretaries of Sections— 25th.

Death

We regret to report the loss by death of Mr. A. Highley, who had been a member of the Society for over fifty years.

How the World looks to a Colour-defective

The question: "Do we really know what the colour-defective person sees?" can be answered affirmatively. The technical data from the researches of Wright and others can be converted into demonstrations by which the normal person sees the world through a colour-blind's eyes. At a meeting of the Physical Society Colour Group held in London on 5th March 1958, Commander Dean Farnsworth (United States Naval Research) showed, and discussed the making of, a short colour film, sections of which had been specially processed to reduce full colour reproduction to the colours in which the same scene appears to colour-defectives of various types and degrees. The colours had been checked by a unilateral deuter-anope. It was interesting to see how bright colours weaken and become indeterminate under colour-defective conditions. The film also demonstrated the Farnsworth lantern and the pseudoisochromatic colour-vision tests.

Planck Centenary

Max Planck, whose quantum theory has been so important to the understanding of the interaction between matter and radiation, was born on 23rd April 1858 at Kiel, when the town was still in Denmark. He spent fifty years at the University of Berlin, and died at Göttingen in 1947.

Improvement of Cotton Strains

According to *Industrial and Engineering Chemistry* (**50**, 25A (Jan. 1958)) sodium $\alpha\beta$-dichloroisobutyrate, when sprayed on cotton plants, has the effect of sterilising their male organs and thus preventing self-pollination. Then superior strains can be crossed, and in some cases actual modification of the cotton molecule can result.

New Chinese Fibre

Reports from Peking (summarised in the *Textile Recorder*, **75**, 57 (Feb. 1958)) indicate that Chinese scientists have shown the fibre from a wild plant, *kender*, a member of the dogbane family, to be superior to cotton, flax, ramie, and wool in tenacity and fineness. Attempts are being made to cultivate the plant, and the resulting fabrics are expected to be cheap and suitable for suitings and shirtings. The fibre has been named "lop linen".

Gordon Research Conferences

The Gordon Research Conferences for 1958 will be held from June 9th to August 29th in New Hampshire, U.S.A., at Colby Junior College (New London), New Hampton School (New Hampton), and Kimball Union Academy (Meriden).

The Conferences were established to stimulate research in universities, research foundations, and industrial laboratories. This purpose is achieved by an informal type of meeting consisting of scheduled lectures and free discussion groups. Sufficient time is available to stimulate informal discussions among the members of a Conference. Meetings are held in the morning and in the evening, from Monday to Friday, with the exception of Friday evening. The afternoons are available for participation in discussion groups as the individual desires. This type of meeting is a valuable means of disseminating information and ideas which otherwise would not be realised through the normal channels of publication and scientific meetings. In addition, scientists in related fields become acquainted, and valuable associations are formed which result in collaboration and cooperative effort between different laboratories.

It is hoped that each Conference will extend the frontiers of science by fostering a free and informal exchange of ideas between persons actively interested in the subjects under discussion. The purpose of the programme is not to review the known fields of chemistry but primarily to bring experts up to date as to the latest developments, analyse the significance of these developments, and provoke suggestions as to underlying theories and profitable methods of approach for making new progress. In order to protect individual rights and to promote discussion, it is an established rule of each Conference that all information presented is not to be used without specific authorisation of the individual making the contribution, whether in formal presentation or in discussion. No publications are prepared as emanating from the Conferences.

Individuals interested in attending a Conference are requested to send their applications to the Director. Each applicant must state the institution or company with which he is connected and the type of work in which he is most interested. Attendance at each Conference is limited to 100.

The complete programme of the Conferences has been published in *Science* for February 28th.

Requests for attendance at the Conferences, or

for any additional information, should be addressed to W. George Parks, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island, U.S.A. From 9th June to 29th August 1958 mail should be addressed to Colby Junior College, New London, N.H., U.S.A.

The Conference for the week of 7–11th July 1958, under the chairmanship of Dr. E. I. Valko, will be concerned with textiles, and will discuss such topics as tension changes in textile structures during wetting and drying, new results in wool chemistry, movement of fluids in fibrous beds (capillary sorption and permeation), and the transport of liquids in textile assemblies.

New Books and Publications

Light, Colour, and Vision

By Yves le Grand (translated by R. W. G. Hunt, J. W. T. Walsh, and F. R. W. Hunt). Pp. xiii + 512. London: Chapman & Hall Ltd. 1957. Price, 63s. 0d.

This book is based on a series of lectures on physiological optics given at the Institute of Optics, Paris, by the author, who is the Honorary Secretary of the Commission Internationale de l'Éclairage (C.I.E.). It deals with light and colour from the standpoint of the eye as a receptor of radiant energy. Most of the book (15 chapters) is taken up with experimental facts, and the rest (5 chapters) with theories of vision.

Fundamental topics such as radiant energy and sources of radiation are followed by chapters on the eye as a visual receptor and on retinal illumination, leading to the basic principles of colorimetry. This section includes a detailed discussion of stimulus values, introducing an account of the work of Maxwell, Wright, and Guild on reference stimuli. The equations for changing from one system to another are given in detail, and although this is not an easy section to follow for the reader with only a general knowledge of the subject, any difficult concepts are thoroughly explained. For example, the statement that "any mono-chromatic light is equivalent to the algebraic sum of suitable amounts of these reference lights" is shown only to be correct if it is appreciated that one of the reference stimuli is negative.

On the other hand, many interesting topics are discussed which the typical reader of this *Journal* will have little difficulty in following. Thus the chapter dealing with the basic principles of colorimetry contains references to colour tempera-ture, complementary colours, colour filters, and additive and subtractive colour mixing. Also, those who are interested in the present work of Stiles and others, on the redetermination of the standard observer using a 10° field instead of the 2° field used by Wright and Guild, will appreciate Chapter 9, *The Colour Vision of Real Observers*. The next five chapters deal with various aspects of colour threshold, viz. "that luminance below which colour becomes no longer discernible", and contains subject-matter with which the average colourist is not familiar, although it does refer to night blindness, colour tolerance, colour flicker, and the effect of glare on difference thresholds. Chapter 15, which completes Section A, deals with anomalies of colour vision and contains on p. 335 a diagrammatic attempt to explain the inheritance of anomalous colour vision.

Whereas Section A is written essentially from the point of view of the physicist, Section B (*Theories of Vision*) incorporates elements of anatomy, physiology, and psychology deemed necessary to understand the various visual theories which have been put forward. The retina is discussed in great detail in three chapters dealing with its anatomical, photochemical, and electro-physiological aspects. Chapter 19 (*Theories of Colour Vision*) is extremely interesting and discusses the recent work of Granit on the retinal receptors in animals. He believes that information about brightness and colour is carried from the retina to the geniculate ("jointed") body by units he calls *dominators* and *modulators*. The former merely inform the centres in terms of brightness and are much more numerous than the modulators, which are considered to be responsible for colour discrimination. Granit finds seven modulators, but they lie in three groups, viz. red, green, and blue–violet bands, the grouping of which is in general agreement with the trichromatic theory of colour vision. He also thinks that there is some evidence in favour of the existence of three different receptors corresponding to the red, green, and blue–violet primaries, and differing in the diameter of the nerve fibres. In the frog these nerve fibres vary considerably in diameter, and it is thought that the thickest fibres correspond to the red modulators. Müller's theory of the difference between protanopia and deuteranopia is also very intriguing. He claims that the former is a retinal defect, whereas deuteranopia arises from a defect of the fibres of the optic nerve, which explains why diseases which affect the conduction of the optic nerve always produce a deuteranopic, never a protanopic, defect.

In his treatment of the subject, the author uses an abstract approach which is complementary to some recent American books and which is more difficult to comprehend by the reader not possessing the necessary mathematical, physical, and anatomi-cal background. Nevertheless, the volume contains a great deal of information for the dyer and colourist, and will be valuable as a reference book. It has been very well translated, and possesses a a good index and an excellent bibliography.

F. Jordinson

Pigment Particles
Their Character and Behaviour in Paint

Teddington: Research Association of British Paint, Colour and Varnish Manufacturers. 1956. Pp. 74. Price, 7s. 6d.

The Research Association of British Paint, Colour and Varnish Manufacturers, better known from the name of its headquarters as "The P.R.S.", has long carried out studies of pigments and their characteristics as part of its research programme.

The results of its work are normally confidential to members, but the Council has not infrequently released for publication accounts of work of very wide interest. Now a grant of money from the Counterpart Fund of United States Economic Aid has enabled and encouraged the P.R.S. to publish an excellent little book in which many of the observations they have made on pigments over a number of years are collected and related to the properties and behaviour of paint.

In the very early days of electron microscopy the P.R.S. constructed its own electron microscope, realising what a powerful tool it might be in pigment research. The increase in magnification given by the electron microscope as compared with the optical microscope immediately revealed a gamut of particle shapes which often went a long way to explain particular properties. The booklet is well illustrated with a selection of photographs, admirably arranged to illustrate the many facets of pigment preparation and behaviour which are dealt with.

Chapters covering particle characteristics, the effect of method of preparation on the properties of some pigments, and wetting and dispersion are followed by three chapters on paint as a fluid, paint as a film, and finally durability.

Although the work of several departments of the P.R.S. is covered, one simple lucid style of presentation is maintained throughout.

One word of criticism: the examination of organic pigments has received scant attention by comparison with inorganic pigments, and a somewhat out-of-balance impression of the range of pigments used in paint may thereby be given.

This should not be allowed to obscure the fact that *Pigment Particles* is the best 7s. 6d. worth published on pigments. It could and should be read with advantage by everyone concerned with the preparation and use of pigments.

D. M. STEAD

Costing in the Bleaching, Dyeing and Printing Trade

Published under the auspices of the Textile Finishing Trades Association. Pp. x + 67. London: Sir Isaac Pitman & Sons Ltd. 1957. Price, 21s. 0d.

Cost accountancy is a branch of economics, the dismal science, and the authors have produced a reference book of costing for the textile trade which is as taut and businesslike as one would expect from a conclave of accountants. This is no disparagement of the book: on the contrary, the Textile Finishing Trades Association is to be congratulated most highly on this, the first attempt to define and set out the framework of a costing system recommended to the finishing industry. No textile-finishing works should fail to obtain a copy, and there is much information, e.g. on steam usage, which other industries may find interesting and profitable to study.

The book is most courageous in that it leans very strongly to the side of "historical costing", now somewhat old-fashioned, against the modern trend for standard costs, and it produces powerful arguments in favour of this heresy. The strongest argument, not mentioned, perhaps, for reasons of modesty, is that several acknowledged experts in the costing world cannot fit the trade to cherished dogma: the orthodox become heterodox. We hope that the purists in the accountancy profession will sustain them in their dilemma. Textile finishing, although becoming more and more scientific in its application, is aesthetic in its appeal and service; there are the imponderables of handle, texture, and beauty of colour and design, which cannot as yet be confined to standard costs.

To return to the book: there is a brief outline and definition of the system. It is recommended that the works are divided into process cost centres and service cost centres, and that direct labour, direct material, and direct expense plus the requisite overheads are allocated to process cost centres. Works or production overheads are charged to either type of centre, and other overhead costs are charged direct to product costs as recommended. All points are fully amplified, and the build-up of the cost of the final product is made clear.

The problem of activity level is discussed, and it emphasises the need for a normal measure to be determined An extremely thoughtful point mentioned is the question of interest on capital—whether it should or should not be included as an item of cost. In fact, the different aspects of overheads, such as fixed and variable, selling, advertising, and research, are fully covered. The chapter with special notes on water, steam, and power cost is simply first-class, and the advice about depreciation and maintenance sound.

All in all, this is a very valuable little book, quite worth its weight in folding money, especially to the smaller firm, whose costing resources are limited but which seeks a sound basis for costing. To would-be cost accountants in textile finishing it is as necessary as a primer; to managers in fact and in embryo, it is an acquisition.

The Textile Finishing Trades Association and the authors deserve the warmest thanks, not least from the aesthetes in the trade, whose "interpretations" are, unfortunately, subject to the scrutiny of cost analysis.

JOHN E. H. BENNETT

The Book of pH

By R. B. Webber. Pp. 111. London: George Newnes Ltd. 1957. Price, 30s. 0d.

On p. 26 of this book we are reminded of the nursery rhyme: "What are little girls made of?", and on p. 46 a coloured picture shows an indicator changing colour when added to acid or alkali. Starting at such an elementary level, the

author imperceptibly leads the reader into the topic, and by means of a large number of beautifully coloured pictures and diagrams makes sure that no-one can possibly not understand.

But this is not all. All the theoretical ideas are systematically introduced and explained, starting from simple atomic structure and leading to a description of electrode processes. Graphs and tables are used to ensure that each point is adequately conveyed before going on to the harder theory.

At the end of the book there are appendixes with some simple mathematical explanations of what logarithms are, examples of how to calculate results, and a useful glossary of technical terms.

No-one now has any excuse for pleading ignorance of this topic, unless he or she cannot afford 30s. 0d. and is too lazy to borrow the book from the Society's library.

L. PETERS

Statistical Methods in Research and Production
with special reference to the Chemical Industry

Edited by Owen L. Davies. 3rd edition 1957. Pp. xii + 396. London: Oliver & Boyd. Price, 45s. 0d.

There is a widespread mistaken belief that statistics can be used to prove anything: in fact, it is impossible for statistics to prove anything. All that statistics can do is to show what is the probability that the data obtained can have arisen by mere chance. It does not even tell us what numerical improbability ought to be taken as impossibility, nor does it show how to achieve absolute certainty. It is up to the non-statistician to take the risk of making a wrong decision: all the statistician can do is to say what the risk seems to be, on the evidence presented.

On this basis, there seems to be no need to bother with such a useless subject. But as long as the above limitations are appreciated, there are many advantages which it has to offer. It makes one thoroughly understand the need to assess what risks one is taking, to evaluate the evidence on an objective system instead of "by scowl of brow".

The book under review offers a systematic outline of the mathematical techniques at present widely used in other industries but not yet common in the field of textile coloration. It will seem heavy going for most readers of the *Journal* because of its very comprehensive and detailed treatment of the subject, but it is on that account most valuable as a work of reference.

There are numerous examples, such as how to apply control tests to check the quality of production, the use of confidence limits to assess the reliability of a newly trained analyst, the analysis of variance as a means of tracking down the sources of variability, the problem of proper sampling methods, and other practical examples from actual experience.

The scientist who wishes to discover the "best" curve to fit his data will find in the book a complete scheme of calculation to obtain linear or curvilinear regression lines.

Several detailed tables are given of statistical parameters for testing whether results are significant or not, and a nomogram is included for graphically interpolating values intermediate between those obtainable from the tables.

Unfortunately, the tables are not easily understood without reference to the text, and the nomogram seems of little value, since ordinary interpolation is all that is needed in practice. Nevertheless, this minor criticism should not detract from the rest of the work, which is highly to be recommended for any scientific library in industrial research.

A sequel to the first edition (1947), entitled *The Design and Analysis of Industrial Experimentation* (1956, 63s. 0d.), by the same editor and publishers, is essential as a supplement to the present edition.

L. PETERS

Facts from Figures

By M. J. Moroney. 2nd edition 1953. Pp. 472. Harmondsworth: Penguin Books Ltd. Price, paper 5s. 0d., cloth 8s. 0d.

Recently in the *Journal* a statistical analysis was made of the reliability of colour-fading tests [1]. As a result, interest has been aroused, and the need recognised for a wider understanding of the techniques employed, so that the validity of such conclusions could be assessed and, perhaps, so that other applications might be discovered. This interest in statistics led to a proposal that an Explanatory Paper be published on the subject, but the existence of the above book makes this unnecessary. Written by one talented author, it is delightfully readable even though all the arithmetic needed is given. By skipping the calculations, one can still follow the argument, and the book can be read almost like a novel. One of the chapters has the title *How to be precise though vague*, and this indicates the tone of the whole book.

Its scope is wider than is usual with bulky textbooks. Even an advanced treatment of ranking methods is included, the theory of which will be invaluable, for much of the work of readers of the *Journal* is concerned with results not yet expressible in numerical units but capable of being arranged in an order of magnitude.

The author does not attempt to do everything nor to be exhaustive in what he does do, but he really aims at giving enough information to satisfy someone taken on a tour of the statisticians' workshop and to let him see enough of the job to learn something. The reader will finish up with more than a smattering of the jargon, and a good idea of the work that can be tackled and the tools available for the different tasks. Moreover, he will be able to understand the limits as well as the possibilities in clear statistical thinking.

I can give no higher praise to this book than to say that I wish I had written it.

L. PETERS

[1] Bülow, U., and Horrdin, S., J.S.D.C., **73**, 459 (1957).

Methoden der organischen Chemie
(Houben–Weyl)
Band I/1
Allgemeine Laboratoriumspraxis
Teil 1

Edited by Eugen Müller. 4th edition 1958. Pp. xliii + 1048. Stuttgart: Georg Thieme Verlag. Price, DM 198.00.

For the 4th edition of this compendium, general laboratory practice has been dealt with in two volumes, of which the present is devoted to the science and processing of materials, while the second will contain analytical methods. Matters of exclusively technical interest are excluded from this volume, but borderline cases receive attention.

During the last decade, the number and the scope of general working methods— the tools of organic chemistry— have been enormously extended; one has only to reflect on such very recent processes as those under the extreme conditions of high vacua or great pressure, molecular distillation, chromatography, use of inclusion and double compounds, and ion exchange, while electrophoresis has now assumed great importance. Gas chromatography, however, is reserved for a future volume, because of its present extremely rapid development. The subject-matter is dealt with in twenty-nine chapters— *Varieties of Glass* (with their chemical, physical, mechanical, optical, and electrical properties, including glasses for apparatus tubing, thermometers, electrodes, and special permeability to light); *Unions in Glass Apparatus* (both elastic and rigid); *Ceramic Materials* (including hard porcelain, gas-tight unions, chamotte, oxide ceramics, porous filter and diaphragm substances; *Metallic Materials in Laboratory Practice* (with their general properties, precautions to avoid corrosion, strength, and the corrosion properties of iron, various steels, aluminium, lead, copper and its alloys, nickel and its alloys, platinum, silver, tantalum, titanium, carbon, and graphite, also tables giving corrosion data for 66 chemical reagents); *Use of Synthetic Materials in the Laboratory* (these include thermoplastic substances and those capable of degrees of hardening, and elastomers, all with their mechanical and thermal properties and degree of stability towards corrosion); *Cements and Adhesives*; *Storage of Chemicals*; *Stands and Supports for Apparatus*; *Separation Methods— Decantation, Filtration, and Ultrafiltration* (including filter media, aids to filtration, and filter devices); *Washing, Clarification, and Decolorisation* (embracing physical, chemical, and special processes, with the properties of active carbons and charcoals, bleaching agents, gels, and ion-exchangers for decolorisation); *Presses*; *Breaking of Emulsions* (including processes by thermal, freezing, dilution, mechanical (stirring, filtration, centrifugal, vibrational), electrical, radiation, and chemical (influence of electrolytes and demulsifiers) methods; *Distribution and Extraction* (with 110 pages of comprehensive theoretical treatment and laboratory practice); *Crystallisation*; *Preparation and Methodical Use of Inclusion Compounds*; *Isolation of Substances by Formation of Complex and Double Compounds*; *Salting out* (with

application to carboxylic and sulphonic acids, dyes, and soaps); *Isolation, Purification, and Separation by Adsorption from the Gaseous State; Ion Exchangers* (74 pages, which also contain the fundamental theory of the subject); *Redox Resins, Centrifuges; Dialysis and Electrodialysis; Preparative Electrophoresis* (in homogeneous and heterogeneous media with use of carriers); *Drying of Solids; Distillation and Rectification* (with comprehensive theoretical treatment); *Evaporation; Distillation and Sublimation in Moderate to High Vacua* (including drying by refrigeration); and finally a synopsis of work dealing with *The Design and Equipment of Organic Chemical Laboratories*. Each of these 29 chapters is provided with its own special bibliography, and altogether there are 517 diagrams and illustrations.

The mere sight, let alone the reading, of this book gives real pleasure, since all the sections are written by those who obviously know their subject; the treatment is thorough but not diffuse, while the diagrams, indexing, printing, and binding are excellent. Some realisation of the magnitude of this volume may be gained from the fact that the author index contains 34 pages of names in three columns, and the subject index occupies 51 double-column sides; it will be welcomed by all who are interested in the subject.

H. H. HODGSON

Methoden der organischen Chemie
(Houben–Weyl)
Band XI/1
Stickstoffverbindungen II
Amine
1. Herstellung

Edited by Eugen Müller. 4th edition 1957. Pp. lviii + 1178. Stuttgart: Georg Thieme Verlag. Price, DM 208.00.

Owing to the enormous growth of the chemistry of the amines it has been necessary in this 4th edition to divide the subject-matter, and consequently this first volume deals only with methods for the preparation of amines. Other changes have been to treat aliphatic and aromatic types as a whole and not in separate compartments, since preparation methods for individual amines in both classes are identical in most cases, and, on the same grounds, a classification into primary, secondary, and tertiary amines has been considered to be inexpedient. It is pointed out also that the alkylation and dealkylation of amines appear where required, and are not assembled in a chapter devoted to amine transformations.

All the sections have been written by experienced chemists of the Farbenfabriken Bayer AG., Leverkusen, so that the volume is enriched by numerous hitherto unpublished methods, devices, and data from the laboratories of this works. Moreover, the literature has been searched up to 1956, and such references as have been tested by the reviewer are found to be accurate in every case.

Prefaced by an introduction to the chemistry of the amines, separate chapters of the book deal with the different methods of obtaining amines— direct introduction of the amino group, and

amines from exchange and addition reactions, by reduction and condensation, via organo-metallic compounds, and by transformation reactions and cleavage. The special methods discussed in Chapter IX include alkylation by ammonia or reaction of amines with olefins, carbon monoxide, and water; N-alkylation by hydrogen cyanide and nitriles; cyclisation of nitriles; reaction of hydrogen cyanide sesquihydrochloride with aromatic hydrocarbons; aromatisation of enamines; amines from azides; cleavage and rearrangement by reduction of cyclic β-oxo-amines. Amines may be prepared from other amines with preservation of the amino group e.g. by exchange and elimination of functional groups, nuclear alkylation of aromatic amines, preparation and transformation of unsaturated amines, and dehydrogenated dimerisation of amines. The last two of the twelve chapters deal with the preparative separation of primary, secondary, and tertiary amines (by physical and chemical processes) and with the properties and handling of ammonia.

This class of compound is one of the most important in organic chemistry, so that it is not surprising that the author index should occupy 79 pages of names in three columns, and that there is a subject index of 63 double-column pages. Further, it is safe to predict that almost every individual organic chemist engaged in research will consult this volume periodically, and that the appearance of the various volumes of this 4th edition of Houben–Weyl, after the long interval of some 25 years since the publication of the 3rd edition, will be received everywhere with gratitude.

H. H. HODGSON

New Books received

Marking Containers of Hazardous Chemicals. 2nd edition 1958. London: Association of British Chemical Manufacturers. Pp. vi + 108. 10s. 0d. ($2.50).

Emulsions. Theory and Practice. American Chemical Society Monograph Series No. 135. P. BECKER. New York and London: Reinhold Publishing Corpn. and Chapman & Hall Ltd. 1957. Pp. x + 382. 100s. 0d. ($12.50).

Lithopone. E. A. BECKER. Stuttgart: Berliner-Union GMBH. 1957. Pp. 154 + 56 Figures + 18 Tables. DM 32.00.

The Visual Pigments. H. J. A. DARTNALL. London and New York: Methuen & Co. Ltd. and John Wiley & Sons Inc. 1957. Pp. vii + 216 + 1 halftone plate. 30s. 0d.

The Manufacture of Lakes and Precipitated Pigments. A. W. C. HARRISON (Revised by J. S. REMINGTON and W. FRANCIS). 2nd edition 1957. London: Leonard Hill (Books) Ltd. Pp. xx + 284. 30s. 0d.

Comptes rendus de la Dix-neuvième Conférence XIX—Paris 16–25 Juillet 1957. Basle: International Union of Pure and Applied Chemistry. 1957. Pp. 174 + 1 plate.

Symposium on Trade Wastes and Report of Discussions. London: Institute of Sewage Purification. 1957. Pp. 112 and 55. 10s. 0d.

Present Day Views on Mechanism of Leather Dyeing and their Practical Value. G. H. OTTO. Ludwigshafen: Badische Anilin -und Soda-Fabrik AG. [1956]. Pp. 32.

Textile Chemicals and Auxiliaries with special reference to Surfactants and Finishes. Revised and edited by H. C. SPEEL and E. W. K. SCHWARZ. 2nd edition 1957. New York and London: Reinhold Publishing Corpn. and Chapman & Hall Ltd. Pp. vi + 545. 108s. 0d.

A History of Industrial Chemistry. F. SHERWOOD TAYLOR. London: William Heinemann Ltd. 1957. Pp. xvi + 467 + 22 plates. 30s. 0d.

Naturally Occurring Quinones. R. H. THOMSON. London and New York: Butterworths Scientific Publications and Academic Press Inc. 1957. Pp. viii + 302. 50s. 0d. ($9.00).

Elementary Practical Organic Chemistry. ARTHUR I. VOGEL. London: Longmans, Green & Co. Ltd. Part II—Qualitative Organic Analysis. 1957. Pp. x + 349–644 + i–xxiv. 21s. 0d. Part III—Quantitative Organic Analysis. 1958. Pp. xiii + 645–840 + i–xxxii. 21s. 0d.

Manufacturers' Publications and Pattern Cards

The Society does not accept any responsibility with regard to the statements in the following notes.
Any publication abstracted may be referred to by members of the Society on application to
Dr. C. B. Stevens, Dyeing Department, Leeds University

Imperial Chemical Industries Ltd.

The following data sheets have been issued for insertion in the pattern card *Procion Dyestuffs in Textile Printing*—

PROCION BLUE HB— This reactive dye gives bright greenish blues of excellent fastness to light when printed on cellulosic fibres. It is suitable for use alone and also as a basis for browns, greens, and greys. A minimum steaming time of 5 min. is recommended for optimum fixation. The recommended recipe for white resists is based on Resist Agent PR. Fastness figures on cotton include— Light 6–7, washing (Test No. 5, 5 times at 100°c.) 4–5.

PROCION BRILLIANT ORANGE HGR— This reactive dye gives bright oranges when printed on cellulosic fibres. A minimum steaming time of 5 min. is recommended. The colour becomes very much redder and duller on after-coppering. It is not recommended for resists using Resist Agent PR. Fastness figures on cotton include— Light 4–5, washing (Test No. 5, 5 times at 100°c.) 4–5.

PROCION BRILLIANT RED H7B— This reactive dye gives bright bluish reds when printed on cellulosic fibres. It is readily dischargeable at all depths, and white resists may be obtained with Resist Agent PR. It gives very stable print pastes. Fastness figures on viscose rayon

include— Light 5, washing (Test No. 5, 5 times at 100°c.) 4–5.

PROCION BRILLIANT RED 5B— This reactive dye gives bright bluish reds, much bluer than Brilliant Red 2B and possessing better building-up properties. It is recommended for supplementing the 2B brand, particularly when using non-steaming fixation processes. Fastness figures for a print on cotton include— Light 4–5, washing (Test No. 5, 5 times at 100°c.) 3–4.

PROCION BRILLIANT YELLOW H5G— This reactive dye is primarily designed for printing on cellulosic fibres to give bright greenish yellows. It is also recommended for producing bright greens in combination with the Procion blues. Optimum fixation requires a minimum of 5 min. steaming. It is readily dischargeable in all depths. Fastness figures for a print on viscose rayon include— Light 6–7, washing (Test No. 5, 5 times at 100°c.) 3.

PROCION RUBINE H2B— This reactive dye gives bluish reds when printed on cellulosic fibres. A minimum of 10 min. steaming is recommended for fixation. It is suitable for use alongside direct dyes subsequently to be aftercoppered, but should not be used alongside Soledons and is not recommended for resists based on Resist

Agent PR. Fastness figures on viscose rayon include— Light 6–7, washing (Test No. 5, 5 times at 100°c.) 3–4.

PROCION SCARLET H3G— This reactive dye is primarily of interest in self-colour, giving bright scarlets when printed on cellulosic fibres. It requires a minimum of 5 min. steaming on cotton and 10 min. on viscose rayons for optimum fixation. It may be used alongside Soledons but not on Brenthol prepares. The colour becomes much duller on aftercoppering. It is not recommended for resists with Resist Agent PR. Fastness figures on cotton include— Light 4, washing (Test No. 3, once at 85°c.) 3–4.

PROCION YELLOW HA— This reactive dye gives bright golden yellows and builds up easily to yield deep colours. Unlike Procion Yellow R it may be printed on Brenthol AS and related Brenthols and on Brenthol AT without adding sulphite. White resists may be obtained with Resist Agent PR. Fastness figures on cotton include— Light 6–7, washing (Test No. 5, 5 times at 100°c.) 4–5.

PROCION RED G— This data sheet, 4:02B, replaces the previous issue under this number giving fastness data for dyeings on cotton and rayon.

TECHNICAL INFORMATION LEAFLETS— *Dyehouse No. 392. The Dyeing of Terylene–Cellulosic Fibre Unions*— Four general procedures are recommended— (a) A two-bath method using disperse dyes and either vat, azoic, or reactive dyes. (b) A single-bath method using disperse and direct dyes. (c) A high-temperature, single-bath method. (d) For blacks, a method using direct dyes for the cellulosic fibre and either disperse dyes or azoic combinations for the Terylene. (e) A padding procedure using solubilised vat dyes which give reasonably solid dyeings of good fastness in pale depths. The material is padded with a solution of the dye and sodium nitrite at 40–60°c., repadded, without drying, through sulphuric acid at 20–60°c., washed off, and soaped. Recipes are given for producing a range of British Colour Council colours using the various procedures together with corresponding fastness data.

Dyehouse No. 399. Vulcaprene A: Applications in the Leather Industry.

Dyehouse No. 407. The Dyeing of Terylene Polyester Fibre–Wool Blended Materials— Supplement No. 2— A modified method of dyeing such mixture cloths in enclosed winch machines is recommended. The reduction–clear is

dispersed with, and pale to medium depths may be produced in a single bath. By using Dispersol AC instead of Lissapol C or Lissapol D the staining of the wool is reduced. The substantial disperse-dye stain remaining is now removed by soaping with Lubrol E.

Dyehouse No. 411. The Dyeing of Triacetate–Wool Unions — Single- and two-bath methods may be employed using either disperse or azoic dyes for the triacetate and Propolan, acid-milling, or chrome dyes for the wool. Staining of the wool by the disperse dyes is best controlled by using Dispersol AC. With pale or bright dyeings where the staining is only slight, Lissapol C or D is still recommended, since retained Dispersol AC may subsequently cause browning on exposure to light. When using a two-bath method to produce medium to full depths it is recommended that Lubrol E be added to the second dyebath.

Dyehouse No. 413. Standard Depths for Fastness Testing — With the establishment by the E.C.E. of three additional standard depths for fastness testing ($\frac{1}{3}$, $\frac{1}{6}$, and $\frac{1}{12}$ standard depth) to supplement the existing range (2, 1, and $\frac{1}{3}$ standard depth) already accepted by both the E.C.E. and I.S.O., the complete range and the official descriptions will be used in future publications. Light-fastness assessments will be made at 2, 1, and $\frac{1}{12}$ standard depth, which are illustrated in *The Fastness Assessment of Textile Dyestuffs* (2nd edition) as "azoic combinations", "normal depths for all fibres", and "pale depths for all fibres" respectively. It should be noted that $\frac{1}{12}$ refers to the amount of dye actually present on the fibre compared with the 1/1 standard and not that initially present in the dyebath, which is the customary method of expressing the depth of a dyeing.

Rubber No. 50. Coloration of Polyurethane Flexible Foam by Dyeing— Such foams may be dyed with fast-to-milling acid dyes at 80–90°c. in presence of sodium sulphate. The total volume of dye solution should be just sufficient to fill the voids in the foam: excess free solution promotes uneven dyeing. A silicone anti-foaming agent is used to prevent formation of bubbles when the foam is squeezed under the surface of the solution to release air from the voids. Although the wet fastness of the dyeings is inferior to that of mass-pigmented foams, deeper colours can be obtained by the dyeing process.

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., 68, 23 (*Jan. 1952*) *and also, together with symbols and the periodicals abstracted, in the annual index*

I— PLANT; MACHINERY; BUILDINGS

PATENTS

Dye Vessel
D. Fornelli   USP 2,779,183

A U-shaped dye vessel has serrated sides, the projecting parts of the serrations on each side being opposite one another. The upward sides of the projections are at < 45° and the downward sides at > 45° to the vertical. This arrangement creates greater turbulence in the dye liquor and results in better penetration.   C.O.C.

Embossing Machine for Textiles
Associated Dye & Print Co.   USP 2,756,669

A pattern roller is placed between and acted upon by two pressure rollers at least one of which is slidable relative to the sides of the machine. The pattern roller has a flexible metallic surface having a pattern on it. Rollers supplied by the sides of the machine's frames engage the pattern roller, they are coaxial with the pressure rollers and with them form a cage in which the pattern roller is supported. Upon pressure being exerted by one of the pressure rollers on the pattern roller the other rollers coact to cause flexing of the surface of the pattern roller so as to emboss cloth being pressed between a pair of the rollers. The pressure is applied through the slidable roller. This results in very uniform embossing. The system is readily incorporated into many existing machines with little modification of them.   C.O.C.

———

Pad–Jig System of applying Vat Dyes to Linen Cloth (VIII p. 441)

III— CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Textile Chemicals Table
S. Jost   *Textil-Rund.*, 13, 89–99 (Feb. 1958)

A number of specialities for sizing, desizing, wetting, scouring, bleaching, stripping, levelling, dye-fixing, and printing are classified with respect to manufacturer, constitution, and application.   S.R.C.

Relationship between Constitution and Activity of Antistatic Agents
M. Bühler   *Textil Praxis*, 12, 1142–1149 (Nov.): 1234–1245 (Dec. 1957)

The author discusses problems connected with static electricity in the textile industry. The technique of measuring electrostatic charge is described. Details are given of experimental work involving a number of anti-static agents. It is postulated that the lowering of the charge is brought about by polar substances which increase the dielectric constant of the fibre–air interface. The usual antistatic agents have poor fastness to washing. Methods of obtaining durable results are indicated. Forty-nine references are given.   L.A.T.

PATENTS

Colloidal Dispersion of Dextran for Finishing Textiles
Commonwealth Engineering Co. of Ohio
         USP 2,756,160

Textiles can be sized and stiffened effectively and conveniently by use of pure dextrans having a range of

molecular structural repeating α-1:6- to non-α-1:6-linkages ratios between 1·9 : 1 and 30 : 1, mol. wt. of 5,000 to 150×10^6 (determined by light-scattering measurements), and able to form colloidally stable, aqueous solutions or dispersions of 0·5–5·0% by weight at ordinary temperatures.   C.O.C.

Water-repellent Compositions comprising a Polysiloxane, a Urea- or Melamine-Formaldehyde Resin and a Curing Agent
General Electric Co.   USP 2,757,152

A mixture of (a) an organo polysiloxane containing no Si-bonded hydrogen and in which the organic groups are attached to Si by C-Si bonds, < half of the organic groups are CH_3, the remainder being CH_3, C_2H_5 or C_6H_5, (b) an incompletely polymerised urea- or melamine-formaldehyde condensate; and (c) an organic or organometallic salt of Ti, Zr, Sn, Pb, Al, Zn, Ni or Sr, imparts a water-repellent finish which withstands a large number of launderings or dry cleanings.   C.O.C.

Fungicidal Compositions comprising Copper-8-quinolinolate with Heavy Metal Salts of Alkylphosphoric Acid Esters
Sun Chemical Corpn.   USP 2,756,175

Copper-8-quinolinolate is heated in an organic solvent with a heavy metal salt of a mono- or di-alkyl acid ester of a phosphoric acid. The solutions are used for rot proofing cellulosic textiles. Thus mono-dioctyl acid orthophosphate (60), nickel acetate (40) and xylene (110) are refluxed until clear, the water and acetic acid formed being removed by azeotropic distillation. Copper-8-quinolinolate (22) is then added and the whole refluxed till a clear dark green solution is obtained. The product is diluted with xylene before being used.   C. O.C.

Guanylmelamine Pyrophosphates for Imparting a Flame-resistant Finish to Cellulosic Materials
American Cyanamid Co.   USP 2,779,691

Salts of guanylmelamine with pyrophosphoric acid inhibit flame propagation in porous cellulosic materials. They are used alone or in combination with resinous binders.   C.O.C.

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Mechanism of Light Absorption of Complexes having Electrostatic Bonds
Á. Kiss

Acta Chimica Academiae Scientiarum Hungaricae, **10**, (4), 373–386 (1957):

Hungarian Tech. Abs., 9, (4), 107 (1957)

A theory has been evolved by which the mechanism of the light absorption of electrostatic complexes can be uniformly interpreted. As shown by group-theoretical calculations, the manner of term cleavage depends on the number of odd p and d electrons, on the multiplicity of the basic term, and on the symmetry of the field of force. The correlation consists in the decrease of symmetry leading to maximum term cleavage. In the case of p^5 and d^5 electrons no term cleavage occurs with any kind of symmetry of the field. Prohibited transitions between the subterms of the cleaved term cause the light absorption in the visible, near-infrared, and ultraviolet regions. If the three factors determining the manner of term cleavage remain unchanged, the number of b bands is identical, independent of the number of charges on the central atom or of the chemical composition of the complex.   C.J.W.H.

Reaction of Sulphonation
XLIV— Isomerisation of Benzenedisulphonic Acids
S. P. Starkov and A. A. Sprýskov

J. Gen. Chem. U.S.S.R., **27**, 3067–3071 (Nov. 1957)

The effect of concn. of sulphuric acid and of temp. upon the isomerisation of m-benzenedisulphonic acid is studied, and it is shown that the optimum conditions are 90% H_2SO_4 at 206°c., or 87% at 235°c. Isomerisation of o-benzenedisulphonic acid at 233°c. occurs very readily (93% after 2·5 hr.). Isomerisation of m- and p-benzenedisulphonic acids occurs more slowly; at 235°c. and 87% H_2SO_4 equilibrium is reached only after 200 hr. (equilibrium mixture 66·3% *meta* + 33·7% *para* isomer).

XLV— Determination of the Isomers of Chlorobenzenesulphonic Acids
A. A. Sprýskov and O. I. Kachurin

Ibid., 3072–3075

Methods for the determination of the isomeric chlorobenzenesulphonic acids have been evolved on the basis of m.p. curves of the binary systems o- and p-chlorobenzenesulphonyl chlorides, and the *meta* and *para* isomers. Determination of the amount of the *para* isomer in the ternary system o-, m-, and p-chlorobenzenesulphonyl chloride was made by the above technique. The quantitative replacement of the chlorine atom in chlorobenzenesulphonic acids by the methylamino group followed by bromination allows determination of the *meta* isomer in a mixture of chlorobenzenesulphonic acids.

XLVI— Equilibrium between Toluenesulphonic Acid and its Acid Chloride
A. A. Sprýskov and Yu. L. Kuz'mina

Ibid., **28**, 184–187 (Jan. 1958)   G.J.K.

Bromination of 2:7-Dihydroxynaphthalene
R. G. Cooke, B. L. Johnson, and W. R. Owen

Chem. and Ind., 1623–1624 (14 Dec. 1957)

Direct substitution of 2:7-dihydroxynaphthalene (I) gives two dibromo deriv., which are each reduced to 3-bromo-2:7-dihydroxynaphthalene by $SnBr_2$ in acetic acid. Authentic 3:6-dibromo-2:7-dihydroxynaphthalene is obtained by allowing I to react with either 3 or 4 mol. of Br_2 and then reducing with Sn and HBr in acetic acid; it is not identical with either of the deriv. above, which are held to be the 1:6- and 1:8-dibromo-2:7-dihydroxynaphthalenes respectively. Rearrangement is found to be involved in the reduction of the two latter dibromo cpd. to the same monobromo deriv. This orientation is of interest because of the reversibility of certain electrophilic substitutions at reactive and crowded positions in aromatic cpd.   H.H.H.

Kinetics of the Bromination of some Aromatic Amines
R. P. Bell and E. N. Ramsden

J.C.S., 161–167 (Jan. 1958)

Measurement of redox potentials enabled the rate of bromination of NN-dimethyl-aniline, -o-, -m-, and -p-toluidine and of NN-diethyl-o-, -m-, and -p-toluidine to be followed in strongly acid soln. (e.g. $1-8$ $M \cdot H_2SO_4$), with bromine concn. in the range $10^{-7}–10^{-2}$ M. The observed rates decrease rapidly with increasing acid concn., and, by using the acidity functions of these soln., the second-order velocity constants for the reaction between the bromine and mol. are found to lie in the range $10^8–10^{10}$ litre-mole^{-1}-sec.$^{-1}$. NN-Diethyl-m- and -p-toluidine are more reactive than the corresponding dimethyl cpd., but NN-diethyl-o-toluidine reacts at about one-quarter of the rate of the dimethyl cpd., presumably because of the greater steric effect of the ethyl groups.   H.H.H.

Oxidation of Aromatic Amines. VI— Persulphate Oxidation of some Carcinogenic Aromatic Amines
P. Sims

J.C.S., 44–47 (Jan. 1958)

Persulphate oxidations of 2'-chloro-4-dimethylamino- and 4-dimethylamino-2'-methyl-*trans*-stilbene, 4-dimethylamino-azobenzene and -diphenyl, NN-dimethyl-1- and -2-naphthylamine, 3:4:1-xylidine, and sulphanilamide are described; the principal products are the sulphuric esters of the corresponding o-aminophenols, which yield the free o-aminophenols on acid hydrolysis, viz. 2'-chloro-4-dimethylamino- and 4-dimethylamino-3-hydroxy-2'-methyl-*trans*-stilbene, 4-dimethylamino-3-hydroxyazobenzene, 4-dimethylamino-3-hydroxydiphenyl-, 1-dimethylamino-2-naphthol, 2-dimethylamino-1-naphthol, 2-amino-4:5-dimethylphenol, and 4-amino-3-hydroxybenzenesulphonamide. Persulphate oxidations of 4-dimethylaminostilbene itself, 2-aminofluorene, 4-amino-4'-fluorodiphenyl, 2-amino-anthracene, -anthraquinone, and -chrysene, and 4-aminoazobenzene were unsuccessful.   H.H.H.

Kinetics and Mechanism of Diazotisation. XIII— Relationship of Diazotisation to General Acid–Base Catalysis
H. Schmid and C. Essler

Mh. Chem., **88**, (6), 1110–1112 (1957)

The velocity coefficients (at 25°c.) now recorded for the diazotisation of o-, m-, and p-chloroaniline, aniline, and

o-, *m*-, and *p*-toluidine can be expressed by the relationship

$$\log k = 11{\cdot}089 + 0{\cdot}178 \; K_B$$

where k is the velocity coefficient and $K_B = [\text{R·NH}_3^+]$ $[\text{OH}^-]/[\text{R·NH}_2]$. This expression is analogous to that given by the general acid–base catalysis hypothesis of Brönsted, as shown by the close agreement of the experimental and calculated data. H.H.H.

Nitrosation, Diazotisation, and Deamination
I— Principles, Background, and Method for the Kinetic Study of Diazotisation
E. D. Hughes, C. K. Ingold, and J. H. Ridd
J.C.S., 58–65 (Jan. 1958)

Diazotisation is shown to depend kinetically on a process ending in N-nitrosation to form a nitrosammonium ion, all subsequent steps being fast; and the process leading to nitrosation is found to consist of several steps and may take a number of alternative courses depending on the nitrosation carrier. These carriers are considered in relation to the kinetics to which they should give rise, and it is shown that there is not a one-to-one correlation. As a result, a variety of kinetic forms have to be demonstrated and transitions traced between them, before any certainty can be attained as to the carriers. Attempts are made to reconcile many apparent disagreements which occur in the earlier history of diazotisation kinetics, and the conditions to be satisfied in an experimental kinetic investigation are considered. It is emphasised that, in a reaction between members of Brönsted acid–base systems, a clear distinction must be kept between stoichiometric and molecular rate-constants.

II— Second- and Third-order Diazotisation of Aniline in Dilute Perchloric Acid
E. D. Hughes, C. K. Ingold, and J. H. Ridd
Ibid., 65–69

The diazotisation of aniline and other aromatic amines has been found to be kinetically of the second order by some previous investigators and of the third order by others; no one has hitherto reconciled these observations, and it is now shown that the difference of kinetic result is connected with acidity. The overall kinetic order of the diazotisation of aniline in dilute perchloric acid falls, as the excess of acid is reduced, from 3 to near 2, and finally rises to about 2·6 as the last of the excess of acid is removed. It is concluded from the data that the fall owes nothing to the acid–base equilibria to which the reactants are subject, and must therefore be of primary significance for the mechanism of diazotisation; it is due to a fall of order in aniline from 1 to 0, the kinetic order in nitrous acid being always 2. These kinetics account for nearly all the reaction, though signs of a small acid-catalysed component can be seen.

III— Zero-order Diazotisation of Aromatic Amines in Carboxylic Acid Buffers
E. D. Hughes and J. H. Ridd
Ibid., 70–76

The diazotisation of aniline in acetate and phthalate buffers near pH 5, with a constant excess of nitrous acid, follows linear reaction–time curves until the falling conc. of aniline approaches 10^{-3} M. At higher aniline conc., the kinetic order is 0 in aniline; and, by comparisons among different runs, it is 1·8 in nitrous acid, the defect below 2 being explicable as a buffer disturbance. The zeroth-order law applies, not only to aniline, but also to substituted anilines with $pK_a >$ about 4, which all undergo diazotisation at the same absolute rate. For more weakly basic aniline deriv., however, the rate falls, and a non-zero order in amine enters, these effects increasing as the basic strength is diminished. Analogies with previous work on nitration and chlorination are pointed out. In first approximation, acetate and phthalate buffers do not change the kinetic orders in amine or nitrous acid, but a part of the rate in their presence is represented by a catalytic term of first order in buffer anion. There is probably a superposed small disturbance, of a type serious with some other buffers, and characterised by a loss of kinetic order in nitrous acid in substitution for an introduced non-zero order in buffer acid.

IV— Hydrogen-ion Catalysis in the Diazotisation of *o*-Chloroaniline in Dilute Perchloric Acid
E. D. Hughes, C. K. Ingold, and J. H. Ridd
Ibid., 77–82

The diazotisation rates (sometimes observed), which are greater than those prescribed by the kinetic equations of the preceding papers, are shown to be due to an additional diazotisation process, which could be made dominating with an amine of suitable basicity, by operating in a suitable range of acidity, with a very low conc. of nitrous acid. This new process, when applied to *o*-chloroaniline in perchloric acid in 0·005–0·020 M. excess, with nitrous acid in conen. below 0·0001 M., gives a reaction of first order each in hydrogen ions, in amine, and in nitrous acid.

V— Catalysis by Anions of Strong Acids in the Diazotisation of Aniline and of *o*-Chloroaniline in Dilute Perchloric Acid
E. D. Hughes and J. H. Ridd
Ibid., 82–88

Perchlorate, nitrate, and apparently fluoride ions do not catalyse diazotisation, although chloride, bromide, and iodide ions do so, with an importance increasing in this order. Previous work by Schmid gives the kinetics as of first order each in hydrogen ion, amine, nitrous acid, and halide ion, and conditions have now been adjusted in the attempt to give reactions of zeroth order in amine, whilst remaining of first order in each of the other reactants; this consists in building up a sufficiently high conen. of a sufficiently reactive free amine in the acid required by the catalysis. The attempt failed for chloride catalysis, failed with aniline for bromide catalysis, but succeeded with the weaker base *o*-chloroaniline, and was completely successful with iodide catalysis. It is shown that the process made rate-controlling in this way is completely independent of the process made rate-controlling when the kinetics of the uncatalysed reactions are similarly modified (cf. Part II).

VI— Comparative Discussion of Mechanisms of *N*- and *O*-Nitrosation with special reference to Diazotisation
E. D. Hughes, C. K. Ingold, and J. H. Ridd
Ibid., 88–98

Apart from the common basic step of conversion of nitrous acid into its conjugate acid, any one of the steps of production, or interconversion, of the nitrosating agents, or of the attack by any of them on the amine, may be made rate-controlling, the overall kinetics changing accordingly. No step after that which first implicates the amine ever becomes rate-controlling. In weakly acidic aq. media, the important carriers are nitrous acidium ion, dinitrogen trioxide, and nitrosyl chloride, bromide and iodide, but not nitrosonium ion, dinitrogen tetroxide, nitrosyl carboxylates, or nitrous acid. Nitrosonium ions are not produced, and nitrous acid is present but useless. Nitrosyl carboxylates nitrosate nitrite ion more easily than they nitrosate amines, and thus they catalyse nitrosation of the latter by way of dinitrogen trioxide. Recent literature on the kinetics of *N*- and *O*-nitrosation is reviewed, and some discrepancies are explained. For example, Okano and Ogata's claim for HN_2O_2^+ as a main nitrosating agent in aq. diazotisation arises from their not controlling kinetic form before calculating rate-constants. Most other difficulties can be traced to the fallacy that buffers do nothing except control pH. Dusenbury and Powell's discrepant results for deamination arise from unrecognised catalysis by their phosphate buffer, which produces the nitrosating species NOH_2PO_4 and NOHPO_4^-. Anbar and Taube's similarly discrepant results for the nitrosation of water, as followed by oxygen exchange, arise from the same cause. Other modern work is cited, however, which agrees well with that now recorded.
H.H.H.

Neutral Diazo Compounds
I. V. Grachev, G. G. Gusev, and D. Z. Zavel'skii
J. Gen. Chem. U.S.S.R., **27**, 2820–2829 (Oct. 1957)

The preparation of various compounds of the type I has been carried out by condensation of the sodium salts of phenylnitrosamines Ar·NNa·NO with diazonium chlorides. I is shown to exist in aqueous and alcoholic solution in equilibrium with the diazonium cation and the nitrosoaminate anion—

$$\text{Ar–N=N–N–Ar} \rightleftharpoons \text{ArN}_2^+ + \text{Ar–N}^-$$

NO		NO
(I)	(II)	(III)
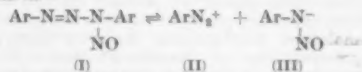
II couples with naphthols, whilst III only is converted into the coupling form by the addition of acid. G.J.K.

Tautomerism of the Salts of Aminoazo Compounds
I. N. Zhmurova

J. Gen. Chem. U.S.S.R., **27**, 2704–2710 (Oct. 1957)

Spectroscopic investigation of a large number of aminoazo dyes—

$$(CH_3)_2N-\langle\ \rangle-N=N-R$$

many of which are new, has been carried out in neutral and acid solution. Of the two possible positions for salt formation (amino and azo nitrogens) those dyes with substituents in the 2′ position form salts on the dimethylamino grouping. This result is explained on the basis of the steric effect upon the azo linkage of the substituent in the 2′ position.   G.J.K.

Physical Properties of the Aminoazobenzene Dyes. IV— Position of Proton Addition
E. Sawicki

J. Org. Chem., **22**, 365–367 (1957):
Chem. Abs., **52**, 1086 (25 Jan. 1958)

The basicity and absorption of some azo dyes were correlated with the position of proton addition to these dyes. Further spectral evidence is given for the tautomer concept of proton addition to the 4-aminoazobenzene dyes. Addition of a proton to $p\text{-}C_6H_5N{:}NC_6H_4N(CH_3)_2$ (I) gave 2 tautomers: The ammonium or A tautomer, where the proton added to the $N(CH_3)_2$ group and was apparently iso-pi-electronic with $(C_6H_5{:}N)_2$ (II); and the cationic resonating or C tautomer, where the proton added to the β-N atom. Addition of a proton to $p\text{-}(pHOC_6H_4N{:}N)$ $C_6H_4N(CH_3)_2$ gave a mixture of tautomers. The A tautomer must be iso-pi-electronic with $p\text{-}C_6H_5N{:}NC_6H_4OH$; the C tautomer was shown by the band at 548 mμ. In acidic solution of 4-aminoazobenzene dyes the tautomeric equilibrium was displaced so that a second proton could add to give the dicationic tautomers, C' and A', respectively. The C' tautomer involves a high energy resonance structure containing a quinone ring and 2 adjacent charges. The excited state of A' has a comparatively low energy resonance structure involving a quinone ring and 2 well separated positive charges. The ultraviolet spectra were determined for dyes $C_6H_5NNC_6H_4X$ when X = $4\text{-}NH_2$, $3\text{-}NH_2$, H, $4\text{-}N(CH_3)_2$, $3{:}4\text{-}CH_2((CH_3)_2N)$ and $4\text{-}N(CH_3)_3I$.   C.O.C.

Adsorption and Partition Methods in the Separation of the *ortho* and *para* Isomers of Sulphonated Hydroxyazo Dyes
O. A. Stamm and H. Zollinger

Helv. Chim. Acta, **40**, 1105–1123 (Aug. 1957)

The potential use of the methods of paper chromatography, paper electrophoresis, and the Craig countercurrent separation technique are discussed with reference to their application in the dyemaking industry. The successful separation by these methods of 2- and 4-arylazo-1-naphtholsulphonic acids is described, and the difference between partition and adsorption is clearly shown. Since the 2 and 4 isomers are both adsorbed by paper, it is clear that such dyes, contrary to generally accepted views on the substantivity of simple azo dyes, are substantive to cellulose.   J.E.B.

Effect of Ring Fusion on *o*-Hydroxyazo Compounds
E. Weiss-Berg and R. Wizinger

Helv. chim. Acta, **40**, 1056–1059 (June 1957)

The visible absorption band of 1-hydroxy-2-phenylazonaphthalenes is moved hypsochromically on fusion of a benzene ring at the 3:4 positions, while corresponding annelation at the 3:4 positions of the 2-hydroxy-1-phenylazonaphthalenes causes a bathochromic shift of the visible absorption band.   J.E.B.

Azo Dyes from Substituted 2-Aminothiophens
J. B. Dickey, E. B. Towne, M. S. Bloom, W. H. Moore, B. H. Smith, and D. G. Hedberg

J.S.D.C., **74**, 123–132 (March 1958)

This paper concerns the effects of the position and the nature of substituents on the colour of azo dyes derived from 2-aminothiophens. Of primary interest is the colour shift from the red of phenylazo dyes to the greenish blue of the analogous 5-substituted 3-nitro-2-thienylazo dyes. The greenish blue of 2-amino-3-nitro-5-acyl(or aroyl)-thiophen dyes is in striking contrast with the violet–red of 2-amino-5-acylthiophen dyes and the violet of dyes from 2-amino-3:5-bismethylsulphonylthiophen. Even

simple aniline coupling components afford blues to blue–greens with the 5-substituted 2-amino-3-nitrothiophens. However, progressively increased bathochromic shifts to bluish green are obtained with the following coupler types — tetrahydroquinoline, benzomorpholine, and 2-alkoxy-5-acetamidoaniline. Dyes from 2-amino-3-nitro-5-acyl-thiophens, particularly, have excellent affinity for secondary cellulose acetate and give good exhaustion and level dyeing. They colour cellulose acetate deep, bright blues to greens. Dyed fabrics have superior gas-fume fastness, moderate light fastness, and good dischargeability.   AUTHORS
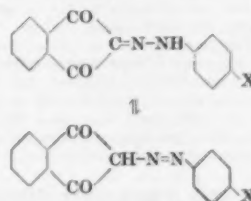
Cyclic Arylazo-β-diketones. I— Condensation of Indane-1:3-dione with Diazonium Compounds
É. Yu. Gudrinietse and G. Ya. Vanag

J. Gen. Chem. U.S.S.R., **28**, 58–62 (Jan. 1958)

A series of 2-arylazoindane-1:3-dione derivatives are prepared, with the substituent mainly in the *para* position in the benzene ring, although *ortho-* or *meta-*substituted derivatives are also listed, e.g.—

(X = Br, NO$_2$, SO$_3$H, and H).   G.J.K.

Spectroscopic Study of Selected Diphenylmethanes and Triphenylmethane Dyes
F. C. Adam

Univ. Microfilms (Ann Arbor, Mich.),
Publn. No. 22154, 132 pp.

Ionisation of Triphenylmethyl Chloride in Nitromethane
Y. Pocker

J.C.S., 240–243 (Jan. 1958)

The work of A. G. Evans *et al.* (*Trans. Faraday Soc.*, **47**, 711 (1951); **50**, 16, 470, 568 (1954); *J.C.S.*, 3803 (1954) and 1020 (1957)) on the ionisation of triphenylmethyl chloride (I) is revised. It has been found that I, on dissoln. in nitromethane (II), instantaneously develops HCl to an extent determined by a simple equation of mass-law type and that this HCl significantly contributes to the electrical conductance of the soln. and is concerned with the development of colour. The addn. of tetraethylammonium chloride completely discharges the colour associated with the carbonium ion, whilst the corresponding perchlorate has no effect. The colour discharge by added chloride ions, taken in conjunction with the experimental observations of Evans *et al.*, indicates that the ionised I when dissolved in II is in the form of free ions, rather than ion-pairs, though the chloride ion is largely combined in, or with, HCl.   H.H.H.

Oxidation of Derivatives of *o*-Phenylenediamine. V— N^2-Substituted Derivatives of Anilinoaposafranine (Rimino Compounds) and Related Compounds
V. C. Barry, J. G. Belton, J. F. O'Sullivan, and D. Twomey

J.C.S., 859–863 (Feb. 1958)

Catalytic hydrogenation of glyoxalinophenazines affords N^2-subst. deriv. (I) of anilinoaposafranines (rimino cpd.) and not N^3-subst. deriv. as stated earlier (cf. *J.C.S.*, 3347 (1956)). Some of these cpd., and others not accessible by the glyoxalinophenazine route, e.g. I (R = C_6H_5, R′ = CH$_3$), have been obtained by reaction of primary amines with anilinoaposafranines; (I) was obtained also by direct alkylation of II (R = C_6H_5). Similar cpd. have been prepared also by condensation of isomers of anilinoaposafranines with some primary amines, and by condensation of 4:5-diarylamino-*o*-quinones with *o*-phenylenediamines. The presence of $>$NH in these cpd. was first suggested (*loc. cit.*) by their relative instability in boiling acetic anhydride and the appearance of a sharp band at 3300 cm.$^{-1}$ in the infrared region, but further work established this band as due to an –NH– group.

(I)   (II)
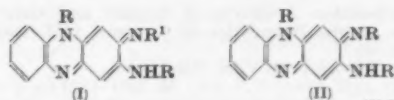
H.H.H.

New Group of Metallochromic Indicators
J. Körbl, V. Svoboda, D. Terzijská, and R. Pribil
*Chem. and Ind.*, 1624–1625 (14 Dec. 1957)

Condensations of glycine with formaldehyde (I) together respectively with the dyes thymolsulphonphthalein (II), o-cresolsulphonphthalein (III), thymolphthalein (IV), o-cresolphthalein (V), and fluorescein (VI), of sarcosine and β-alanine respectively with I, II, and III, of DL-serine with I, II, III, and IV, of DL-α-aminoisobutyric acid with I, II, IV, and VI, and of L-proline with II and III, give a new group of metallochromic indicators. In general, the above sulphonphthalein deriv. react with Cu^{2+} showing a change in weakly acid medium from yellow to intense blue (in the deriv. of thymol blue) and to purple (in the deriv. of cresol red). In the dependence on structure of the amino-acid residue, the reaction is either instantaneous (in the case of glycine, sarcosine, or serine (residue)), or is dependent on time, the max. of colour being reached within ca. 10 sec. (in the deriv. of L-proline and α-aminoisobutyric acid). With Ni^{2+} the reactions are generally time-dependent. In the sulphonphthalein deriv. the sensitivity for Cu^{2+} is dependent on the soln. pH, on the amino-acid residue, and on the sulphonphthalein used for the condensation. Deriv. of phthaleins react with cations only in weakly ammoniacal medium, where they are themselves violet, Cu^{2+} causing either decolorisation or a hypsochromic effect, whereas Ni^{2+} produces an intense blue colour.

H.H.H.

Reaction of Ninhydrin with Cyclic α-Imino Acids
A. W. Johnson and D. J. McCaldin
J.C.S., 817–822 (Feb. 1958)

Structures (I and II) are proposed for the yellow and the purple condensation products from ninhydrin and the cyclic α-imino-carboxylic acids (e.g. proline). Ring size is shown to have a marked influence on the course of the reaction. The purple condensation products are also obtained from ninhydrin and the cyclic bases, and the mechanism of these condensations, which resembles that of the oxidative decarboxylation of α-amino acids, is discussed.
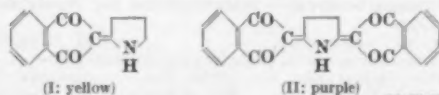
(I: yellow)   (II: purple)

H.H.H.

Photochemistry of the Thiazine Dyes and Instrumentation for Photochemistry
N. Wotherspoon
Univ. Microfilm (Ann Arbor, Mich.)
Publ. No. 22663, 154 pp.

Syntheses of Substantive Dyes of the Diquinoline Series
L. N. Goldyrev
J. Gen. Chem. U.S.S.R., 27, 2837–2840 (Oct. 1957)

Tetra- and hexa-methyl-diquinolines and -diquinolylmethanes have been prepared. A comparison of the properties of these dyes shows the latter to be less substantive to cotton. This lack of substantivity may be due to loss of coplanarity.
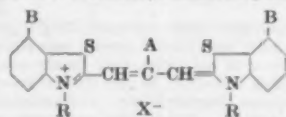
G.J.K.

Cyanine Dyes. XI— Some 7:7'-Dimethylthiacarbocyanines
I. I. Levkoev, N. N. Sveshnikov, E. Z. Kulik, and T. V. Krasnova
J. Gen. Chem. U.S.S.R., 27, 3097–3107 (Nov. 1957)

Preparation of 7:7'-dimethylthiacarbocyanines—

(R = alkyl; A = H or alkyl; B = substituent group; X = anion) is given via 2:7-dimethylbenzothiazole and its quaternary ammonium salt. Isomeric 4:4'-, 5:5'-, and

6:6'-dimethylthiacarbocyanines are prepared in a similar manner. A comparison of the colours of these compounds shows that on going from the 4:4' to the 7:7' isomer the same bathochromic displacement occurs as from the 5:5' to the 6:6' isomer. However, the presence of these groups in the above positions affects the basicity of the dyes and of the benzothiazole nucleus in a different manner. The authors state that these effects cannot be completely interpreted on the basis of electronic displacements.

G.J.K.

Reaction Products of Methylene Bases of Benzothiazole and Benzoselenazole with Alkyl Halides
F. S. Babichev and A. I. Kiprianov
J. Gen. Chem. U.S.S.R., 28, 209–212 (Jan. 1958)

The structure of the reaction products of the addition of methyl iodide to 3-methyl-2-methylenebenzothiazoline and 3-methyl-2-methylenebenzoselenazoline as given by Larrive and Collet (*Bull. Soc. Chim.*, 1443 (1956)) is shown to be incorrect, and in a similar manner doubt is cast upon the structure of the corresponding cyanine dye molecules. An alternative structure (I) is suggested—
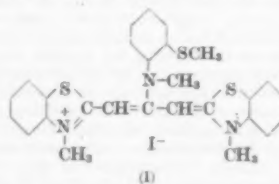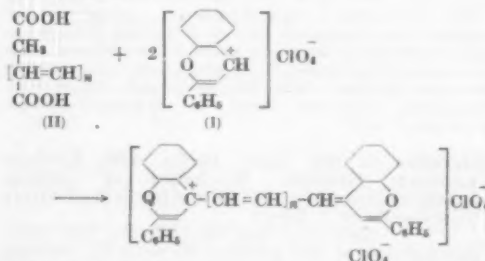

(I)

G.J.K.

Symmetrical Flavylocyanines
R. Wizinger and H. von Tobel
Helv. Chim. Acta, 40, 1305–1310 (Aug. 1957)

Symmetrical flavylocyanines are prepared by condensation of flavylium perchlorate (I) with a vinylene homologue of malonic acid (II) followed by dehydration and decarboxylation—
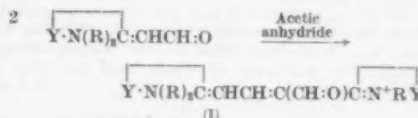

(n = 0–3).

J.E.B.

New Reaction of Formylmethylenic Derivatives of Nitrogen Heterocycles— Structure of Neocyanines
J. Nys and J. Libeek
Sci. et Ind. phot., 28, 433–436 (1957):
Chem. Abs., 52, 937 (25 Jan. 1958)

Formylmethylenic derivatives of N-heterocyclic compounds dissolved in acetic anhydride undergo autocondensation—

(Y = atoms to complete a heterocyclic nucleus; R = Alk). This reaction occurs at room temperature, is accelerated by heat, and enables easy synthesis of trimethincyanine dyes having an aldehyde group in α-position of the chain. I are isolated by converting the acetate originally formed into the less soluble bromide. Presence of the aldehyde group in the chain causes hypsochromic shift in the absorption maximum from that of the corresponding unsubstituted chain compound. Condensing I with heterocyclic quaternary salts containing a reactive group yields neocyanine dyes and the reaction establishes the structure of these dyes.

C.O.C.

Dyes derived from Acenaphthenequinone. XII— 2-(4-Chloro)-thionaphthen-acenaphthylene-indigos

S. K. Guha and A. K. Sinha

J. Indian Chem. Soc., **34**, 771–775 (Oct. 1957)

Vat dyes have been prepared by condensing 4-chloro-3-hydroxythionaphthen with acenaphthenequinone and its 3-chloro, 3-bromo, and 3-methoxy derivatives. All except the methoxy compound are readily reduced with alkaline hydrosulphite at 50–60°c. to yield violet vats from which cotton may be dyed (red dyeings). Comparing the dye from unsubstituted acenaphthenequinone with the corresponding dyes from 5-, 6-, and 7-chlorothionaphthen, there is a hypsochromic shift in the order 5-chloro> 4-chloro > 7-chloro > 6-chloro > unchlorinated dye (Ciba Scarlet G— C.I. Vat Red 45).   A.J.

Quantitative Estimation of the Influence of Substituents on the Absorption Spectra of Planar Molecules— Application to Anthraquinone

H. Labhart

Helv. chim. Acta, **40**, 1410–1420 (Aug. 1957)

The influence of substituents upon the intensity and wavelength of the long-wavelength band of anthraquinone is predicted by a simple perturbation method including cross-terms allowing for specific interaction of two or more substituents. A set of parameters derived from the observed spectra of monosubstituted and disubstituted anthraquinones was used to predict the wavelengths and intensities of other disubstituted and polysubstituted anthraquinones. The parameters were of two types— (1) those characteristic of the substituents, and (2) those characteristic of the position of substitution. Predictions were made within $\pm$ 8 mμ. of the experimental results. A table of spectroscopic data of a large number of anthraquinone derivatives in methylene chloride is given.   J.E.B.

Structure of Chrysenequinone Phenylhydrazines

E. Weiss-Berg and R. Wizinger

Helv. chim. Acta, **40**, 1060–1061 (June 1957)

The 2-hydroxy-1-arylazochrysenes, prepared by coupling an aryldiazonium chloride containing nitro groups with 2-hydroxychrysene, are shown to be different from the compounds prepared by reaction of the corresponding nitrophenylhydrazine with chrysenequinone. These latter compounds, therefore, must be hydroxy-2-arylazochrysenes.   J.E.B.

Reductions in the Isatin Series with Lithium Aluminium Hydride. II— Action of Lithium Aluminium Hydride on Indole and Isatin Derivatives

E. Giovannini and T. Lorenz

Helv. chim. Acta, **40**, 2287–2291 (Dec. 1957)

Investigation of the products obtained by reducing indoxyl, dioxindole, 2:2-dimethylindoxyl, and α- and β-isatoxime showed that the reaction with lithium aluminium hydride proceeds through an indoline-type intermediate.   J.E.B.

Thioindigoid Dyes. Synthesis of Thiophenols and S-Arylthioglycollic Acids

G. M. Oksengendler and Yu. E. Gerasimenko

J. Gen. Chem. U.S.S.R., **27**, 3214–3217 (Dec. 1957)

Aromatic amines, after diazotisation and treatment with sodium polysulphide, yield the diaryl tetrasulphide, which on boiling with NaOH and reduction in an autoclave produces the corresponding thiophenol. Twelve thiophenols have been converted to the corresponding S-arylthioglycollic acids, six of which have not been previously prepared.   G.J.K.

Interaction of Chlorophyll in its Triplet State with Oxygen, Carotene, etc.

E. Fujimori and R. Livingston

Nature, **180**, 1036–1038 (16 Nov. 1957)

Examination of the triplet state of chlorophyll *a* by flash photolysis shows that it is quenched by *p*-quinone, oxygen, α- and β-carotenes, luteol, *Zea* xanthophyll, and *cyclo*octatetraene. Bimolecular quenching constants are given.   A.J.

Flavonoids of the Primulaceae

J. B. Harborne and H. S. A. Sherratt

Nature, **181**, 25–27 (4 Jan. 1958)

Decomposition Products of Sugars and their Influence on the Properties of Caramel (C.I. Natural Brown 10)

A. L. Sokolovskiĭ and V. N. Nikiforova

*J. Appl. Chem. U.S.S.R.*, **30**, 1261–1263 (Aug. 1957)

Chief among the decomposition products of sugars formed in the preparation of caramel are the anhydrides and the inversion products. Small quantities of the products of more complete decomposition of sugars can also be found, such as hydroxymethylfurfural and colouring matters and resinous compounds. The products of condensation (reversion) tend to keep the caramel in the amorphous state; the hydroxymethylfurfural and resinous matter show only a negative effect, increasing the colour and the hygroscopicity of the caramel. The presence of fructose is detrimental, because on heating it very easily changes into hygroscopic products.   T.Z.W.

Chemistry of Bacteria. VII— Structure of Violacein

J. A. Ballantine, C. B. Barrett, R. J. S. Beer, S. Eardley, A. Robertson, B. L. Shaw, and T. H. Simpson

J.C.S., 755–760 (Feb. 1958)

Recognition of the constitution of violacein (I), the violet pigment of *Chromobacterium violaceum* and also of *Chromobacterium*, Strain B.C.1 (from the skin slime of North Sea cod), has been facilitated by its ready methylation with methyl sulphate and potassium carbonate to give a blue cryst. cpd. of mol. formula $C_{23}H_{19}O_3N_3\cdot O\cdot CH_3$ or $C_{22}H_{16}O_3N_3\cdot O\cdot CH_3$, which suggests two possible mol. formulae for I, namely $C_{21}H_{15}O_3N_3$ and $C_{20}H_{13}O_3N_3$. The latter formula offers the more satisfactory explanation of the behaviour of I with alkaline reagents, viz. dissolution in aq. NaOH giving an intense emerald-green soln., which soon becomes red, especially on warming, and leads to the tentatively proposed structure (I). Other structures, based on the C_{21} formula, are briefly discussed.


(I)

H.H.H.
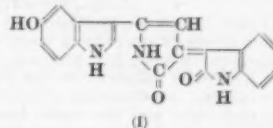
6-Aminocarbostyrils— Intermediates for Azoic and Azo Dyes

American Cyanamid Co.   *USP* 2,754,293

6-Aminocarbostyrils, made by nitration and reduction of suitable carbostyrils, are useful diazo compounds for azoic and other azo dyes. The carbostyrils are made by condensing aromatic primary amines with acylacetic esters or with diketen, to give the arylide, followed by ring-closure in H_2SO_4. Thus *N*-acetoacet-2:5-diethoxyanilide in H_2SO_4 at 85–90°c. gives 5:8-diethoxy-4-methylcarbostyril—
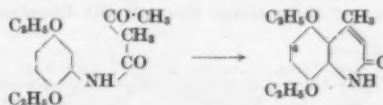

Nitration in acetic acid gives the 6-nitro derivative, yielding the 6-amino derivative (I) by reduction with hydrogen in presence of palladium-charcoal. A diazo solution prepared from I, when used to develop cotton impregnated with 3-hydroxy-2-naphthoanilide gives a deep blue.   E.S.

Monoazo Dyes Soluble in Fats, Waxes, Organic Solvents, etc. and having Water-repellent Properties

Ciba   *BP* 790,797

o-Hydroxymonoazo dyes without SO_3H groups, and containing at least one COOH group, are converted, via their carboxylic acid chlorides, into esters using alkyl or *cyclo*alkyl alcohols of 8–18 C, to give dyes of good solubility in organic solvents, lacquers, etc., and possessing water-repellent properties. Thus the monoazo compound 4-amino-3-nitrobenzoic acid $\rightarrow$ β-naphthol is stirred in chlorobenzene with thionyl chloride. Heating with *iso*-octanol at 120–130°c. then gives the orange dye—
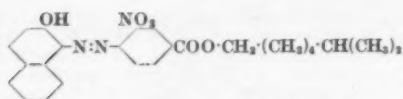
E.S.

Blue, Green, and Olive Metallisable Monoazo Dyes for Wool, Nylon, etc.

Gy *BP* 790,904

β-Naphthylamines substituted on the N atom by an organic radical carrying a substituent capable of chelation are coupled with the diazo compounds of nitro- or alkyl- (or aryl)sulphonyl-o-aminophenols, o-halogeno-(or o-alkoxy)anilines, or suitable cyclic sulphone compounds, to give monoazo compounds which may be metallised in substance, on the fibre, or in the dyebath. Chroming of these dyes in substance, even when SO_3H is not present, readily gives 1 : 1 complexes. The preferred coupling component is N-o-carboxyphenyl-β-naphthylamine (I). Thus 2-amino-4-methylsulphonyl-5-nitrophenol is diazotised in presence of naphthalene-β-sulphonic acid and coupled in presence of acetic acid with I to give—
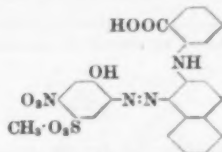

which after drying is dissolved in aq. NaOH and ethylene glycol and heated at 120–125°c. with chromium acetate. The complex so formed dyes wool pure green from an acetic acid bath. E.S.

Monoazo Disperse Dyes having a β-Cyano-β-fluoro-methylethylamino Group

Eastman Kodak Co. *USP* 2,757,173

Diazotised p-nitroaniline and its derivatives, or diazotised 2:4-bis(methylsulphonyl)aniline (I), are coupled with amines—
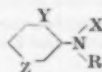
($X = \beta$-cyano-β-difluoromethylethyl or β-cyano-β-trifluoromethylethyl; $R = \beta$-hydroxyethyl, γ-hydroxy-propyl, or $\beta\gamma$-dihydroxypropyl; $Y = H$, OCH_3, or OC_2H_5; $Z = H$, Hal, CH_3, or C_2H_5) to give orange–yellow to reddish-blue disperse dyes. Thus I is diazotised in nitrosyl-sulphuric acid and coupled with N-β-cyano-β-difluoro-methylethyl-N-β-hydroxyethylaniline to give the orange dye—
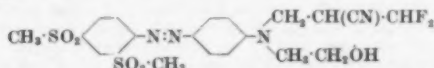
E.S.

Yellow to Red Monoazo Pigments from Dichloro-toluidinesulphonic Acids

American Cyanamid Co. *USP* 2,754,294

The Ca, Sr, and Ba salts of azo compounds obtained by coupling β-naphthol with diazotised 4-amino-2:6-dichloro-toluene-3-sulphonic acid or 2-amino-4:6-dichlorotoluene-3-sulphonic acid (I) are yellow, orange, or orange-red pigments of good light fastness, in contrast to the similar compounds from monochlorotoluidinesulphonic acids, which are reds. Thus 2-amino-4:6-dichlorotoluene is sulphonated at 170°c. in dichlorobenzene with chlor-sulphonic acid, to give I. The Ba salt of the monoazo compound I → β-naphthol is a golden yellow. E.S.

Quaternary Ammonium Salts of N-Heterocyclic Monoazo Dyes— Basic Dyes for Polyacrylonitrile Fibres, etc.

Gy *BP* 791,932

Monoazo dyes made by diazotising an amino derivative of a heterocyclic compound having a 5-membered ring, of which at least 2 members are N atoms, and coupling with a *para*-coupling amine or hydroxy compound, are alkylated to give quaternary ammonium compounds which are basic dyes for polyacrylonitrile fibres, etc. Thus 3-amino-1:2:4-triazole is diazotised and coupled with NN-diethyl-aniline and the monoazo compound is boiled in chloro-benzene with dimethyl sulphate in presence of MgO. The soluble product dyes polyacrylonitrile fibres bright red. E.S.

Metal (Chromium and Cobalt)-complex Dyes for Wool from Mixtures of Monoazo and Disazo Compounds

S *BP* 791,438

Mixed complexes are formed by treating disazo dyes—
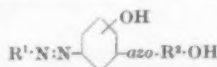
($R^1 =$ aryl of benzene or naphthalene series; $R^2OH =$ residue of a naphthol, pyrazolone, or acetoacetic acid alkylamide or arylamide; the 2 OH groups are in *ortho*-position to azo; a water solubilising group SO_3H, COOH, SO_2Alk, $SO_2·NH_2$, SO_2NHAlk, or sulphonhydroxyalkyl-amide is present) mixed with 1 or 2 monoazo compounds $R^3·N:N·R^4·OH$ or $R^3·N:N·R^5·NH_2$ ($R^3 =$ aryl of benzene series free from SO_3H but containing *ortho* to the azo group a group such as CH_3; $R^4·OH =$ residue of an *ortho*-coupling phenol, naphthol, pyrazolone, or acetoacetic acid alkyl (or aryl)amide, free from SO_3H; $R^5·NH_2 =$ residue of β-naphthylamine free from SO_3H) with metal, e.g. Co or Cr, salts. The products are blues, greens, browns, etc., for wool. Thus the disazo compound 3-amino-4-hydroxy-azobenzene-3'-sulphonamide → 1-carbo-(2'-ethoxy)-ethoxyamino-7-naphthol (28·9 parts) is mixed with the monoazo compound anthranilic acid → 1-m-chloro-phenyl-3-methyl-5-pyrazolone (17·8 parts) and boiled with a Cr complex made from chrome alum and salicylic acid. The product dyes wool and nylon green. Thirty-five examples are given. E.S.

Orange Disazo Acid Dyes from Bis(aminopyrazole) Derivatives

ICI *BP* 791,443

Bis(aminopyrazole) compounds—
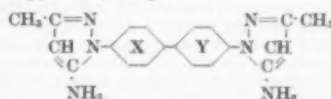
(X and Y may contain CH_3 or OCH_3 groups) are coupled with 1 mol. of diazotised 4-nitroaniline-2-sulphonic acid (I), and 1 mol. of a diazotised aniline or naphthylamine containing 1 or 2 SO_3H groups and optionally OH and/or NO_2 groups, to give bright orange acid dyes applicable from neutral or weakly acid baths. Thus tetrazotised benzidine is reduced to the bis-hydrazine which is con-densed with 2 mol. of diacetonitrile to give 4:4'-bis(5''-amino-3''-methyl-1''-pyrazoloyl)diphenyl, which is coupled first under weakly acid conditions with 1 mol. of diazotised I, and then under alkaline conditions with 1 mol. of diazotised 2:5-dichloroaniline-4-sulphonic acid. Coupling takes place at the 4''-positions. The product dyes wool yellowish orange from a bath containing ammonium acetate. E.S.

Yellow and Orange Disazo Pigments and Azoic Dyes

Ciba *BP* 791,164

Tetrazotised 3:3'-dichloro(or dialkoxy)benzidines are coupled with acetoacetarylides—
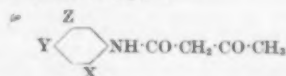
(X = Hal; Y = Hal or acylamino derived from a fatty acid of < 4 C; Z = OCH_3 or OC_2H_5) to give yellow and orange pigments of good fastness to bleeding and to organic solvents when used for instance in pigment printing processes. They may also be made *in situ* on cellulose by the azoic process. Acetoacet-2:4-dichloro-5-methoxyanilide and acetoacet-4-acetylamino-2-chloro-5-methoxyanilide (I) are particularly suitable coupling components. Thus tetrazotised 3:3'-dichlorobenzidine is coupled at pH 4·5–5 with I to give an orange pigment. E.S.

Navy Blue Metal(Copper and Nickel)-complex Trisazo and Tetrakisazo Direct Dyes

S   BP 791,532

Trisazo and tetrakisazo dyes—
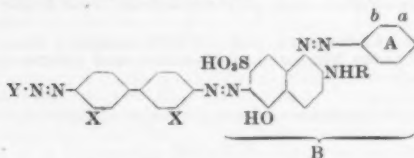
(R = H, Alk, cycloalkyl, aralkyl, or mononuclear Ar; X = chelatable group; Y = B or ortho-coupling naphtholsulphonic acid; a = H or COOH; b = COOH when a = H, and OH when a = COOH; A may contain other substituents), resembling those of BP 760,705 (J.S.D.C., **73**, 67 (1957)) which have o-OH but no COOH in nucleus A, are converted into soluble metal (especially Cu and Ni) complexes, which dye cotton navy blue. Thus the trisazo compound 1-naphthol-3:8-disulphonic acid← dianisidine $\xrightarrow{alkaline}$ N-phenyl-J-acid $\xleftarrow{acid}$ 5-nitro- anthranilic acid is boiled with ammoniacal CuSO$_4$. E.S.

Anthraquinone Intermediates and Dyes

S   BP 790,952

Compounds of formula—
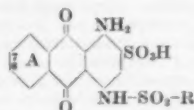
(R = Alk, alkoxyalkyl or arylalkyl; ring A may have Hal in 6 and/or 7 position) are produced by reacting (a) a 1-amino-4-halogenoanthraquinone-2-sulphonic acid with an alkyl-, alkoxyalkyl- or arylalkyl-sulphonic acid amide or (b) a 1-amino-2-halogeno-4-alkyl-, alkoxyalkyl- or arylalkylsulphonylaminoanthraquinone with an alkali-metal sulphite. Reaction (a) occurs in aq. medium at 70–100°c. in presence of an acid-binding agent, e.g. Na$_2$CO$_3$, and a Cu compound, e.g. Cu$_2$Cl$_2$. Reaction (b) occurs in aq. medium, to which phenol may be added, at 100–125°c. under pressure. The products are intermediates for anthraquinone dyes and also are used for dyeing polyacrylonitrile by the cuprous ion process. Reds of good fastness to light and washing are obtained by dyeing or printing cellulose acetate or linear aromatic polyester fibres.   E.T.

Anthraquinone Disperse Dyes

BASF   BP 790,728

Violet to blue dyes for polyester, polyamide and polyurethane fibres are of formula—
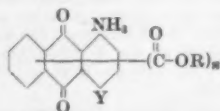

(Y = NH$_2$, arylamino, OH; R = Alk, aralkyl, cycloalk; n = 1 or 2). They are made by esterifying mono- or dicarboxylic acids of 1-amino-, -nitro or -halogeno-4-amino, -hydroxy, -nitro or -halogeno anthraquinones with an aliphatic, araliphatic or cycloaliphatic alcohol followed by conversion of the NO$_2$ or Hal groups to NH$_2$ groups. Thus, 1-amino-4-nitroanthraquinone-2-carboxylic acid chloride (10) and cyclohexanol (100) are heated at 110–20°c. until HCl evolution ceases. The ester crystallises on cooling and is separated by filtration. This product (5·9) is added to SnCl$_2$ (14) in conc. HCl (14) the temperature rising to 60°c. after which it is boiled, cooled and filtered. The red crystals in water (150) at 60–70°c. are oxidised with air to give a blue product which, on dispersion and dyeing gives a blue fast to gas fumes on acetate rayon.   E.T.

Red Anthraquinone Vat Dyes

CFM   BP 791,304

Vat dyes giving reds of good fastness are of formula—
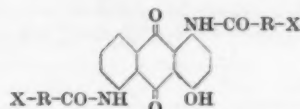
(R = benzene or anthraquinone nucleus; X = Hal or NO$_2$). They are made by condensing a 1:5-diamino-4-hydroxyanthraquinone with ≮ 2 mol. of an aromatic carboxylic acid, X-R-COOH. The starting material is prepared by hydrolysing a 1:5-diacylamino-4-alkoxyanthraquinone with H$_2$SO$_4$. Thus, 1-benzoylamino-4-methoxy-5-(p-toluenesulphonamido)anthraquinone (10) is heated with 90% H$_2$SO$_4$ (100) for 2 hr. at 100°c. Then a mixture of o-dichlorobenzene (300), 1:5-diamino-4-hydroxy-anthraquinone (6·4) and m-fluorobenzoylchloride (11·9) is heated for 12 hr. at 160°c. The dye which crystallises on cooling is filtered, washed with o-dichlorobenzene and then with methanol and dried.   E.T.

Dyeing of Polyesters with Anthraquinone Disperse Dyes

DuP   USP 2,757,064

Bright violet dyeings on polyester fibres which are fast to light are obtained by carrier or pressure dyeing techniques using—
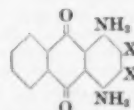

(X = Cl or Br). The light fastness contrasts with that of dyeings using 1:4-diaminoanthraquinone, which, although fast to light on sec. acetate, is fugitive on Dacron. A dye containing both Cl and Br in the 2:3-positions can be made by reacting leuco-1:4-diaminoanthraquinone (70) in nitrobenzene (384) with mixed SO$_2$Cl$_2$ (81) and Br (46). The mixture is added over 2 hr. at 40°c. and the melt is then heated at 60°c. for 2 hr. Dilution with water (100), filtration and alcohol washing follows.   E.T.

1 - Aminobenzophenonesulphone - 2 - aldehydes or -ketones— Intermediates and Disperse Dyes

BASF   BP 790,587

Intermediates for dyes and disperse dyes of good fastness and great colour strength are produced by the following reactions—
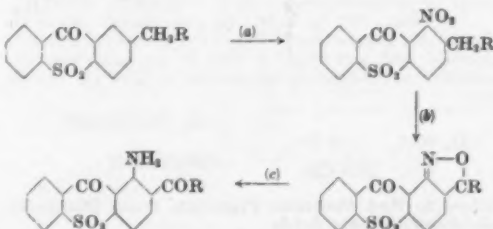
(R = H, Alk, aralkyl, aryl or cycloalk). (a) Nitration in 96% H$_2$SO$_4$ with mixed acids or KNO$_3$ occurs at room temperature or slightly greater to give mono-nitro derivatives which are separated by dilution with water. (b) Conversion to isoxazole derivatives is effected by 60–65% oleum at 0–10°c. the product being separated by dilution. (c) The product from (b) is treated with aq. FeSO$_4$ in H$_2$SO$_4$ at 80°c. to give the 1-aminobenzophenonesulphone derivative which is separated by dilution and filtration.   E.T.

Stabilised Colouring Compositions for Carbon Copying Hectographs, etc.; Manufacture and Use

DuP   USP 2,755,200

Carbinols of lower N-polyalkyl-tri-(p-aminophenyl)-methanes are decolourised and stabilised by interaction with organic bases, e.g. benzyltrimethyl-, or tetramethyl-, or phenyldimethylbenzyl-ammonium hydroxides. The weight of quaternary base used is 2·5–20% of the weight of carbinol to be stabilised. Reaction takes place by heating the carbinol and the quaternary base in a sec. or tert.

aliphatic monohydric saturated alcohol of 3–6 C and the crystals of the product may be advantageously coated with a long-chain (C_{12}–C_{20}) aliphatic compound which is solid at ordinary temperatures but becomes liquid on heating and has b.p. $<$ 150°c. These products are mixed with waxes and applied as a coating on paper giving essentially colourless transfer sheets. In use, colour is redeveloped by acidic reagents which may be incorporated in a separate layer on the coated sheet or may be present in the copy-paper.

USP 2,755,203

Conversion of the colourless, stable leuco-compounds to coloured copy prints is brought about by a developer which has oxidising properties and is acid relative to the *leuco*-form of the trinaryl-methane. Suitable developers are halogenated monocyclic quinones, the corresponding halogenoimides, carboxylic acid peroxides, triarylchloromethanes, alkyl nitriles, volatile liquid iodohalides and N oxides.   E.T.
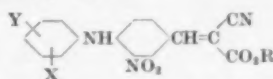
Nitro Diarylamine Methin Disperse Dyes
General Aniline   *BP 790,745*

Dyes giving bright dyeings of excellent wash-, light- and acid-fastness on acetate rayon and Dacron and which also have high affinity are—

(X, Y = H, NO_2, Alk, alkoxy, Hal or $SO_2NR^1R^2$; R^1, R^2 = H, Alk, alkoxy, acyl or may form a heterocyclic ring; R = Alk, halogenoalkyl, OH, or cyano-subst. Alk). They are prepared in 2 stages— (*a*) 4-chloro-3-nitrobenzaldehyde is condensed with an ester of cyanoacetic acid in aq. medium or in an organic solvent with addition of a *sec.* or *tert.* amine as catalyst to give—
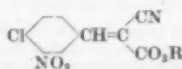
(*b*) The product is condensed with a primary aromatic amine in a solvent or suspension medium with addition of an acid binding agent. Temperatures for both stages may be melt reflux temperatures. Suitable solvents are lower alcohols or ketones, benzene, toluene, etc. and acid binding agents are Na acetate, K_2CO_3, $NaHCO_3$, CaO, etc. Earlier nitro diarylamine dyes were dull, had poor affinity and wash fastness; methin type dyes had poor acid fastness. The present nitro diarylamine methin dyes overcome these weaknesses.   E.T.
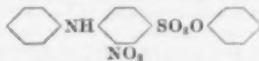
Nitrodiphenylamine Disperse Dyes
Ciba   *BP 790,921*

Yellow disperse dyes, of good light- and wet-fastness on cellulose ester, polyvinyl and polyester fibres are phenylarylamines without solubilising groups which contain, in the same benzene nucleus, an NO_2 group *ortho* to the N bridge and a *para* sulphonic acid arylester group, e.g.—

The intermediate sulphonic acid ester is made by adding to phenol (94) and 1-chloro-2-nitrobenzene-4-sulphonic acid chloride (256) in water (500) at 30–40°c. a solution of NaOH (40) in water (400) at a rate which maintains the pH at 7–8. When reaction is complete, Na_2CO_3 (10) is added and the intermediate separated (m.p. from alc. 71°c.). This intermediate (313·5), aniline (186) and alcohol (1000) are refluxed (80°c.) for 3 hr. The mixture is poured into 30% HCl (250) in water (2500) and the dye is precipitated, separated and crystallised from alcohol (m.p. 112°c.). 62 examples are given.   E.T.

Sulphur-containing Vat Dye
CFM   *BP 791,498*

A vat dye giving a brownish black of good wet fastness and excellent light and weather fastness is produced by treating 2-aminoanthraquinone with S and alkali-metal sulphide at $>$ 250°c. Thus, an aq. suspension of 2-aminoanthraquinone (10), S (20) and 40% Na tetrasulphide (160) is evaporated to dryness with stirring and is then

baked 12 hr. at 280°c. The melt is ground with dil. Na_2CO_3 solution, filtered and washed. The moist cake is stirred with dil. HCl and again filtered and washed. The resulting S-containing vat dye has better fastness properties than earlier similar dyes (*GP* 224,500, 245,768, and 240,792) made by treating aminoanthraquinones with sulphur chloride.   E.T.
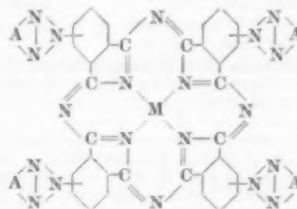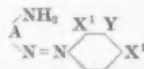
Phthalocyanine Pigments
Gy   *BP 791,359*

Yellow-green to green pigments are of formula—

(A = phenylene, naphthylene or 1:2:3-triazolophenylene radical which is bound at 2 neighbouring C atoms to the N atoms of the triazole ring; M = Cu, Co, Ni or Zn). They are produced by heating, in presence of oxidising agents, unsulphonated o-aminoazo dyes of general formula—

(X^1 or X^2 and Y = carboxyl group or a salt, anhydride, ester, amide, imide or nitrile thereof whilst the other X of X^1 or X^2 = H). This process gives arylotriazolylbenzene-o-dicarboxylic acid derivatives—
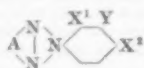
which are the starting materials for the production of the phthalocyanines. The production of the phthalocyanines can, however, be effected in one stage from the azo dye. Thus, 3:4-dicarboxyphenylazo-2′-aminonaphthalene (13·4)—
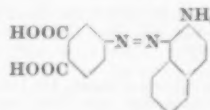
(produced by coupling diazotised 4-aminophthalic acid with 2-amino-naphthalene) is heated at 180–185°c. with urea (14·4), anhydrous $CuCl_2$ (1·5) and NH_4 molybdate (0·2) in nitrobenzene (100). After 4 hr. an intensively green, pure dye is formed which is filtered after 10 hr., washed with nitrobenzene and then with acetone. Extraction with hot dil. HCl and NaOH gives the pure tetra-(naphthotriazolyl)-copper phthalocyanine. The products have high light fastness and are used for colouring lacquers, varnishes, synthetic materials, paints and printing inks as well as for pigment printing of textiles. Soluble derivatives are obtained by sulphonation or by sulphohalogenation and reaction with amines.   E.T.

Yellow Cadmium Sulphide Pigments
FBy   *BP 791,090*

Pigments of excellent fastness to light and very good fastness to weathering are obtained by incorporating into the CdS crystal lattice 0·2–1·0% of Se on the weight of Cd. Thus aq. $CdCl_2$ is mixed with a small amount of Se dissolved in aq. Na_2S and then with aq. BaS and the resultant pigment filtered, dried, calcined at 600°c., cooled, wetground, filtered off, washed and dried. The product is a brilliant yellow fast to light and weathering.   C.O.C.

Cadmium-Mercury Sulphide Pigments
Imperial Paper & Color Corpn.   *BP 791,098*

Pigments which are cheaper, brighter, cleaner and stronger in hue than Cd selenide pigments are obtained by heating, preferably calcining, a mixture of CdS and MgS

to $> 400°c$. in a non-oxidising or reducing atmosphere until the desired colour is developed. The product is not a physical mixture but a combination of the two compounds in a single crystal structure as a solid solution. They may be produced in the "C.P." and "lithopone" types, the former containing no extender and the latter $BaSO_4$ formed *in situ* during their manufacture, e.g. by forming the Cd and Hg sulphides by precipitation of Cd and/or Hg sulphate solutions in presence of BaS.   C.O.C.

Carbon Black (C.I. Pigment Black 7)
Columbian Carbon Co.   *USP* 2,779,664–5
   Production of furnace black of increased absorptive capacity is described.   C.O.C.

Titanium Dioxide (C.I. Pigment White 6)
Societe des Blancs de Zinc de la Mediterranee, E. Chaubary, Pierre Gindre & Cie.

BP 791,302

Na_2TiO_3 is hydrolysed to orthotitanic acid by washing with water at $< 40°c$. The orthotitanic acid is then dissolved by heating with 40–60% aqueous mineral acid in presence of an alkali metal halide (0·5–5·0% on wt. of the orthotitanic acid). This solution is reduced with nascent hydrogen to produce at least a 90% transformation of the Ti to a mineral acid salt of the blue Ti_2O_3. The reduced solution is hydrolysed with boiling water to precipitate most of the Ti as pure, finely divided TiO_2.   C.O.C.

Titanium Dioxide (C.I. Pigment White 6)
British Titan Products Co.   *BP* 791,657
   Rutile TiO_2 is obtained by mixing of $TiCl_4$ vapour with air (1–6 parts oxygen to each part of $TiCl_4$) one or both being heated so that the mixture is at $< 300°c$. irrespective of the heat of reaction. The two separate streams of vapour are passed in the same direction in a reaction chamber so that the $TiCl_4$ stream is admitted within the O_2 stream through one or more ports whose perimeter per unit cross-sectional area is > 26 cm.$^{-1}$. The velocity ratio of the O_2 to the $TiCl_4$ is < 1 and the velocity of each gas is kept so that the Reynolds flow number is < 1800 and < 500 respectively for the $TiCl_4$ and O_2 in the feed ports immediately before entry into the chamber.
   C.O.C.

Behaviour of Various Dyes towards Deinking Chemicals (XI p. 444)

V—PAINTS; ENAMELS; INKS

Stable Suspensions of Spherical Particles— Influence of the Size Ratio of the Dispersed Phase upon Relative Viscosity
G. F. Eveson
J. Oil & Col. Chem. Assocn., **41**, 150–155 (Feb. 1958)
   A rotational viscometer has been used to investigate the influence of the size ratio of the solid phase upon the viscosity of stable suspensions of dispersed rigid spheres. There is only a random variation in viscosity with size ratio. The possible effect which size ratio might have upon viscosity is discussed; the form of the size-distribution curve should have a more pronounced influence than the ratio of diameters of spheres occurring within the suspension.   J.W.D.

Effect of Extender Particle Size on the Gloss of Outside House Paints
B. G. Brand, R. J. Deibert, and E. R. Mueller
Off. Dig. Fed. Paint Varn. Prod. Cl., 30, 74–78 (Jan. 1958)
   The particle-size range of extender materials has an important influence on the gloss and viscosity of outside house paints. Very small and very large extender particles cause loss of gloss, and result in higher and lower viscosity respectively. In the case of a micaceous talc the optimal particle-size range appears to be 7–30 μ., and best results are obtained when particles outside this range are removed. The distribution curve within this range is important; further work is required to ascertain the optimal shape of the curve.   J.W.D.

Zinc Oxide (C.I. Pigment White 4)— A Reactive Pigment
C. T. Morley-Smith
J. Oil & Col. Chem. Assocn., **41**, 85–97 (Jan. 1958)
   The photochemical activity of various types of ZnO are discussed with particular reference to its significance

in determining the durability characteristics of paints. Suggestions are made to explain both the differences recorded between one oxide and another, and the mechanism by which this property may contribute towards the breakdown of a paint film. The soap-forming propensities of ZnO are considered; the effect of these soaps on the various properties of paint films are discussed, and a description is given of experimental work and results aimed at the direct measurement of individual soap formation.   J.W.D.

Design of Heat-reflective Paints
L. M. Tompkins and E. H. Tompkins
J. Oil & Col. Chem. Assocn., **41**, 98–108 (Jan. 1958)
   The theory of light-scattering by fine particles is applied to the design of paint coatings for the reflection of infrared radiation. Commercial white pigments are unsuitable. In order to possess the min. absorption of radiation a pigment must be produced in as high a state of purity as possible and must have nearly perfect crystallites. There is scope for improvement also by the careful selection of particle-size distribution; with a rutile TiO_2 of larger particle-size than usual, reflectivities of infrared radiation of 98% appear possible. Silicon carbide and high-purity Si are potentially outstanding in this application. Most conventional paint vehicles, including cellulose derivatives and the alkyds, have some absorption in the infrared region and are thus unsuitable. Silicones absorb in the near infrared owing to the C–H bonds in the organic parts of the molecule. The polyhalogenoethylenes appear most promising and are discussed at some length.   J.W.D.

Theoretical Aspects of the Chalking of Titanium Dioxide
E. Lund
Färg och Lack, **3**, 57–73 (1957)
   Chalking of TiO_2 in paints is caused by a photoreduction –oxidation cycle initiated by ultraviolet radiation—

$$2TiO_2 + h\nu = Ti_2O_3 + O$$

The released atomic O accelerates the oxidative degeneration of the organic film, which is then removed by weathering, causing unprotected pigment grains to appear on the surface.   C.O.C.

Selective Polar Adsorption and some Rheological Phenomena in Paint Systems
L. Dintenfass
J. Oil & Col. Chem. Assocn., **41**, 125–149 (Feb. 1958)
   The effect of polar adsorption on the dispersion and wetting of pigments and resultant rheological structures is discussed. Thixotropy, viscosity, and yield value of paint systems are reviewed, and the effect of the dilatancy of the paint vehicle is considered. Some criticism is made of former approaches to these problems. Thixotropic recovery time may vary from a fraction of a second to many months. Yield value resulting from pigment structure is considered to be non-existent. It is recognised, however, that flow can take place only when the structure is broken down sufficiently for some free liquid to be present. Viscosity equations are suggested, relating sedimentation vol. and effective (hydrodynamic) vol. of pigments to the relative viscosity of suspensions. Empirical equations are also suggested to cover the rate of thixotropic recovery and time required for mixing (under some conditions). Some aspects of diffusion in paint systems are mentioned, and the diffusion coefficient is suggested to be a time-dependent function. A selective polar adsorption mechanism is shown to play a part in adhesion and corrosion, and quite likely also in the ageing and weathering of paint films.   J.W.D.

Rôle of Pigments in the Forming of Films
F. Kardos, R. Deutsch, and E. Stölczner
Magyar Kémiai Folyóirat, **62** (10), 345–348 (1956): *Hungarian Tech. Abs.*, **9**, (4), 105 (1957)
   The correlation between the rate of sedimentation and the uniformity of coating has been investigated by means of a nitrocellulose varnish containing 40–50 times as much pigment as cellulose nitrate. If the pigment settles quickly, the coating is uniform, whereas if it settles slowly the coating is uneven and spotty. By adding calcium ions to the composition the settling may be accelerated, while the addition of aluminium ions retards the settling and thus the surface characteristics of the film may be influenced.   C.J.W.H.

Printing Ink

W. A. Magie   *USP* 2,754,218

An ink which can be closely controlled as to drying, penetrating and wetting properties comprises a mineral oil, water, a water-soluble dye or insoluble pigment, and either an alkali metal or alkaline earth metal alkylaryl sulphonate, the latter ingredient forming $\ll$ 15% by weight of the ink.   C.O.C.

Inks for Duplicators or Carbon Papers

DuP   *USP* 2,755,201

Stable thin films of essentially colourless N-polyalkyl-tri(*p*-aminophenyl)carbinols, are produced from inks containing in addition to the above and a vehicle, a large proportion of an organic nitrogenous base whose physical state matches that of the vehicle. Thus an ink for carbon paper comprises bleached Montan wax (16·7 parts by wt.), microcrystalline wax (white, melting range 90–95°c.) (12·5), stearylamine wax (22·5), white mineral oil (15·0), petrolatum (12·5), TiO_2 (12·5) and 8·3 parts of the product obtained by treating Crystal Violet carbinol dissolved in *iso*propylalcohol with benzyl trimethyl ammonium hydroxide. Such inks are stable to discoloration on long storage or exposure to humid atmosphere rich in CO_2, do not stain the hands of the person using them, impressions obtained by their use are colourless initially but slowly become deep violet on exposure to the atmosphere or more quickly if they are heated.   C.O.C.

Anti-misting Printing Inks

J. M. Huber Corpn.   *USP* 2,754,219

Inks whose principal vehicle is a hydrocarbon containing an aromatic constituent are prevented from misting when used on high speed presses by adding to them a finely divided organic derivative of montmorillonite in which the organic constituent has a chain of $>$ 11 C, e.g. bentonite treated with 1-hydroxy-(or amino)-ethyl, 2-heptadecenyl glyoxalidine acetate.   C.O.C.

Silicate-based Paint

L. J. C. van de Zande   *BP* 791,806

Paint comprising Na silicate and/or K silicate, Al_2O_3, $Cu(OH)_2$ and/or $BaSO_4$, a pigment and a vehicle is applicable to the most varied materials, e.g. wood, asbestos cement, plaster, stone, glass, metals, etc. It has good covering power and is non-flammable.   C.O.C.

Coatings and Mouldings from Polyglycidyl Ethers

BASF   *BP* 791,836

Polyglycidyl ethers of average epoxy group content $>$ 1 per mol. when hardened with 50–300% of the stoichiometrical amount of a carbocyclic diamine containing two isolated carbocyclic radicals linked by a short chain bivalent bridge radical, each carbocyclic radical having one amino group containing 2 H atoms, the other amino group containing 1 or 2 H atoms, yield alkali-proof coatings even when air-dried on metal which is sensitive to acid. The coatings do not bloom and have good hardness and resistance to water.   C.O.C.

Electron Microscope Study of Accelerated and Natural Weathering (XIV p. 447)

VI— FIBRES; YARNS; FABRICS

Ultraviolet Transmission of Fibre Solutions

W. Schefer

Textil-Rund., 13, 86–88 (Feb. 1958)

Ultraviolet absorption curves were determined for a number of man-made fibres in dimethylformamide and in sulphuric acid, of wool in peracetic acid, of silk, viscose rayon, and cotton in phosphoric acid, and of cellulose acetate in dimethylformamide. Definite maxima are apparent at 275–295 mμ., and radiation of these wavelengths is thus responsible for photochemical damage.   S.R.C.

Degradation of Textile Fibres by Radiation and Heat

A. Sippel

Melliand Textilber., 38, 898–904 (Aug. 1957)

Intrinsic properties such as D.P. determine the stability of man-made fibres towards the action of sunlight, ultraviolet radiation, X-rays, and heat. Metallic compounds present in the polymer as incidental impurities, or purposely incorporated as dulling agents, accelerate photolytic damage of fibres. Quantitative data are given to illustrate the magnitude of these effects.   L.A.T.

Radioactive Degradation of Cotton

O. Teszler and H. Hefti

Textil-Rund., 13, 61–66 (Feb. 1958)

The cuprammonium fluidity and the mushroom head reaction were used to follow the degradation with time of cotton exposed to neutron streams and γ-radiation.   S.R.C.

Degradation of Cellulosic Fibres in Contact with Rusting Iron

W. A. Bell and J. M. Gibson

Nature, 180, 1065 (16 Nov. 1957)

Cotton yarns damped with distilled water and with 0·02% NaCl soln. and wound round steel rods suffered considerable degradation, that in NaCl soln. being most affected. The degradation is explained in terms of the electrode reactions—

$$Fe \to Fe^{2+} + 2e \text{ (anodic)}$$
$$O + H_2O + 2e \to 2OH^- \text{ (cathodic)}$$

i.e. alkaline conditions are generated at the cathodic regions of the corroding iron, thereby permitting the normal alkaline oxidative degradation of cellulose. In accordance with this, cotton in contact with anodic areas (i.e. rust-stained) had a neutral reaction and that from cathodic areas (unstained) was alkaline. If the cotton were impregnated with sulphur so that S^- was formed in place of OH^-, no degradation occurred. Similarly, $MgSO_4$ had a protective effect due to the removal of OH^- as insol. $Mg(OH)_2$.   A.J.

Analytical Studies of Photochemically Degraded Jute— II

W. G. Macmillan and H. P. Bhattacherjee

J. Indian Chem. Soc., 34, 731–738 (Oct. 1957)

The acidic and reducing compounds generated in jute on irradiation by a carbon arc are derived mainly from the lignin component. These acidic products and the uronic acids originally present in the jute have no hydrolytic action and hence do not accelerate the degradation.   A.J.

Examination of the Oligosaccharides isolated from Jute α-Cellulose

W. G. Macmillan, A. B. Sen Gupta, and A. S. Dutt

Nature, 180, 1041 (16 Nov. 1957)

Chromatography of the partial hydrolysate with 0·5 N-H_2SO_4 of jute α-cellulose yielded ten spots due to oligosaccharides (in addition to smaller sugars). Oligosaccharides 1 and 8 (in order of R_f) on complete hydrolysis both yielded galactose, glucose, and xylose with a trace of mannose. No. 6 yielded galactose, glucose, and xylose; and No. 10 glucose, xylose, and possibly traces of mannose.   A.J.

Supercontraction of Wool irradiated with Ultraviolet Radiation or Iodinated

A. R. Haly, M. Feughelman, and J. C. Griffith

Nature, 180, 1064 (16 Nov. 1957)

Wool fibres after ultraviolet irradiation supercontract in Br_2-free LiBr soln. much more rapidly than normal fibres, and the usual two-stage contraction is absent. This effect is not due to cystine links since no further loss of these occurs after 2 hr. irradiation, whereas rate of supercontraction increases up to 20 hr. irradiation. Fibres in which the tyrosine residues were iodinated show a normal first-stage contraction in LiBr soln., but the second stage is extremely slow and similar to that of normal fibres in Br_2-containing LiBr soln. However, irradiated fibres contract rapidly to the final stage in the latter soln. It is suggested that tyrosine takes part in polar or other secondary bonds which can be broken by LiBr.   A.J.

Effect of Sulphuric Acid on Wool

R. L. Elliott, R. S. Asquith, and D. H. Rawson

J.S.D.C., 74, 173–176 (March 1958)

I— Influence of Concentration of Acid on the Histological Attack

The attack of sulphuric acid of various concentrations on wool has been examined under different conditions of temperature and time of treatment. The damaged fibres have been observed microscopically, and results correlated with weight changes and amide-nitrogen analyses. The attack has been shown to be of the following main types—

(1) Hydrolysis in concentrations of acid up to 44% concentrated sulphuric acid by weight. (2) Rapid dissolution in concentrations of acid between 44% and 81·3%, the histological attack being different from the simple hydrolytic attack in (1). (3) A slow attack, at concentrations between 93% and 98%, which becomes considerably more rapid at temperatures above 60°c. (4) A rapid oxidative attack and dissolution, presumably due to free sulphur trioxide, in acid concentrations above 98%. At higher temperatures, all types of attack are more rapid.

Ibid., 176–180

II— The Chemical Attack of Concentrated Acid

Investigation of wool samples after various times o treatment with concentrated sulphuric acid has shown that hydrolysable sulphate increases to a maximum after 1 hr. A fall in sulphate after 1 day to a relatively constant value corresponds to the loss of a scaly membrane. A slow increase in total sulphur is due to removal of the low-cystine-containing fraction of the fibre and to slow benzene-ring sulphonation. Hydrolysates of wool treated with sulphuric acid contain substances identical with those produced on sulphonation of amino acids. Histological changes observed microscopically agree with the results of chemical analysis.   AUTHORS

Arachin Molecule (XII p. 445)

New Preparatory Methods in Electron Microscopy and their Application in Fibre Research (XIV p. 447)

Direct Dye Staining of Viscose Rayon Cross-sections and some of its Applications (XIV p. 448)

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Removal of Alginate-based Sizes
S. Marguier and R. Schutz

Bull. Inst. Text. France (68), 71–75 (June 1957)

Cotton yarns sized with alginate or with starch–alginate mixtures were subjected to various treatments apt to make the alginate insoluble, viz. treatment with metal salts, treatment with formaldehyde, heating, and exposure to light. In most cases, the size was satisfactorily removed from the treated samples during standard handling processes. The exceptions (heating at 120–150°c. for several hours, treatment with solutions containing 1 g. of copper and iron salts per litre) represent conditions not likely to occur in industrial processing.   J.C.F.

Causes of Damage to Polyamide Fibres during Bleaching
D. Wittig

Deut. Textiltech., 7, 312–314 (1957);
Chem. Abs., 52, 1615 (25 Jan. 1958)

Perlon yarn containing 0·106 mg. Fe/g., Perlon yarn treated with ferric sulphate and Perlon yarn freed from iron by treatment with bisulphite acidified with formic acid were all peroxide bleached and then tested for breaking strength, elongation and degree of polymerisation. The results showed that iron is not responsible for the damage done to Perlon during bleaching. The damage seems to be caused by direct oxidation of the amide groups by the peroxide and so to be ascribed to the constitution of the polyamide itself.   C.O.C.

Protection of Polyamide Fibres against Attack by Active Oxygen
K. Dithmar and E. Naujoks

Melliand Textilber., 38, 904–911 (Aug. 1957)

The degradative effect of active oxygen during the hydrogen peroxide bleaching of 6- and 6,6-nylon was investigated. A considerable degree of protection of the fibres against the chemical damage was achieved when bleaching was carried out in the presence of Proventin (Degussa) inhibitors (apparently based on organic cpd. containing two basic nitrogens, at least one of which is NH or NH_2). Experimental results are given in the text.   L.A.T.

PATENT

Bleaching Wood Pulps
Food Machinery and Chemical Corp.   BP 791,352

Bleaching rates can be substantially increased by increasing the bleaching temperature. Unbleached, prebleached, partially purified or unpurified wood pulps, whether chemical or mechanical, at a density of above

10% are treated for not more than 60 min. at 200–280°F. with an alkaline bleaching solution containing a per-compound. Suggested alkalis are sodium silicate, sodium hydroxide and alkaline phosphates or carbonates. Applicable to groundwood, chemigroundwood semichemical, sulphite, Kraft and soda pulps.   R.A.

Pad–Jig System of applying Vat Dyes to Linen Cloth (VIII p. 441)

VIII— DYEING

Substantivity of Dyes and its Causes
A. Schaeffer

Melliand Textilber., 39, 68–74 (Jan.);
182–186 (Feb.); 289–291 (March 1958)

An account is given of experimental work which was designed to evaluate the substantivity of over 450 azo dyes on cotton. An attempt is made to explain substantivity in terms of the chemical structure of dyes with particular reference to conjugation and hydrogen bonding. It is postulated that substantivity is determined by the nature of an undissociated dye molecule and not by its negatively charged anion.   L.A.T.

Physical State of Methylene Blue (C.I. Basic Blue 9) in Dyed Films and its Relation to Light Fading Rates
D. S. E. Campbell and C. H. Giles

J.S.D.C., 74, 164–168 (March 1958)

Methylene Blue in cast films of Cellofas A (ethylmethyl-cellulose) or cast or dyed films of gelatin is present as a mixture of molecularly dispersed and aggregated dye; this is indicated by the detection in the absorption spectra of the peaks of both forms (at ca. 6700 A. and 6200 A. respectively). When irradiated, the aggregated dye fades more slowly than the molecularly dispersed dye. Both forms are found to be present in the film during the actual dyeing operation. Disaggregating agents, viz. phenol, polyvinylpyrrolidone, and urea, reduce the slope of the *CF* ("characteristic fading") curve for the aggregated dye, indicating the production of a narrower range of sizes in the absorbed micelles.   AUTHORS

Degradation of Fluorescent Brightening Agents by Light
E. Elöd and H. Jörder

Melliand Textilber., 39, 61–64 (Jan. 1958)

Fabrics made of different fibres (viscose rayon, secondary cellulose acetate, Perlon, and Rhovyl) were treated with a range of fluorescent brightening agents (Blancophor, Uvitex, and Tinopal). After exposure for increasing periods of time in the Fade-Ometer and in sunlight the intensity of fluorescence was measured with the aid of an ultraviolet photometer. The rate of decrease of fluorescence in Fade-Ometer exposures was about $3\frac{1}{2}$ times as great as in sunlight. The degree of yellowing depends on the type of fibre and on the composition and concentration of the brightening agent.   L.A.T.

Remazol (FH) Reactive Dyes
O. Ziegler

Melliand Textilber., 39, 66–67 (Jan. 1958)

Remazol dyes are a new class of reactive dyes for cotton and regenerated cellulosic fibres. Methods of application in dyeing and printing are described.   L.A.T.

Pad-Steam Dyeing under Laboratory Conditions
K. Döhl

S.V.F. Fachorgan, 13, 54–60 (Feb. 1958)

A compact, self-contained unit is described which is suitable for the dyeing of 10–20 g. of material by the pad–steam technique. Points of importance in translating laboratory results into bulk practice are discussed.   L.A.T.

Measurement of Redox Potentials of Vat Dyes
R. Weingarten

Melliand Textilber., 38, 913–917 (Aug. 1957)

A procedure is described for the measurement and interpretation of reduction potentials of vat dyes. From the shape of the curve the "dyeing" potential can be estimated fairly accurately. The "buffering" capacity of the system depends on the number of reducible carbonyl groups. Fastness to soda boiling appears to depend on the magnitude of the leuco potential, which in the case of anthraquinonoid vat dyes is influenced by the position of the substituent groups but is independent of the dye concentration.   L.A.T.

Dyeing of Zip Fastener Tapes
E. Wilhelm

Textil Praxis, **13**, 70–71 (Jan. 1958)

When dyeing zip fastener tapes in hank form, especially if vat dyes are used, difficulties with regard to penetration and levelness may occur. To obviate this the tapes are wound on to perforated tubes and dyed in enclosed liquor-circulating machines.   L.A.T.

Pad–Jig System of applying Vat Dyes to Linen Cloth
J. N. F. Phillips

J.S.D.C., **74**, 180–183 (March 1958)

A practical description is given of a system of dyeing linen cloth with vat dyes by the pad–jig method, employed in a dyehouse whose annual production exceeds two million yards (for dresses and shirts). Stress is laid on the attainment of the highest possible absorbency during bleaching and other preparatory treatments for dyeing. Details of the padding mangles are given, and the danger of aggregation of dye as a result of the use of unsuitable padding oils is discussed.   AUTHOR

Pad–Steam for Cellulose Triacetate Blends
Celanese Corpn. of America

Technical Bulletin TD–18:
Dyer, **118**, 969 (20 Dec. 1957)

The padding bath is prepared by dissolving a disperse dye in hot triethyl phosphate (10–20 vol.) and then adding hot water (to 100 vol.). Using this liquor for triacetate–cotton blends by a normal pad–steam sequence leaves the cellulose undyed. It is considered that the dye migrates from cellulose to triacetate during steaming.   A.J.

Impact of Man-made Fibres upon the Dyeing Industry
A. H. Wilson

J.S.D.C., **74**, 120–122 (March 1958)

The largest potential field for the expansion of man-made fibres is likely to be the woollen and worsted industries, and dyeing problems will largely determine the extent to which this expansion will take place. The paper gives a survey of the various types of problems which may arise, together with some general indication of the lines of development which are likely to be most fruitful.
   AUTHOR

Dyeing of Nylon Hose
F. Braun

Teintex, **23**, 120 and 123 (Feb. 1958)

In order to attain accurate reproduction of laboratory matching in bulk, the machine should have pH, liquor-ratio, and dye-weight control, together with humidity control in the dye store. Automatic control of the rate of addition of dye and of heating up are required, as well as conditions giving solidity on the panel and top. An arrangement is illustrated in which a photoelectric cell governs the rate of dye addition from a reservoir of concentrated solution. This is claimed to promote levelling.   S.R.C.

Dyeing Polyester Fibres with Palanil (BASF) Disperse Dyes
A. Würz

Melliand Textilber., **38**, 1385–1390 (Dec. 1957); **39**, 74–77 (Jan. 1958)

The Palanils are a new range of disperse dyes for polyester fibres. Their dyeing behaviour and fastness properties are discussed with particular reference to blends of polyester fibres and wool. The all-round fastness properties of such dyeings are impaired if the wool component in the blend is stained with disperse dyes. Suitable methods of clearing the wool in the mixture are discussed. Reference is made to the use of a new carrier, Palatinit M.
   L.A.T.

High-temperature Dyeing of Acrylic Fibres
J. Khachoyan and J. P. Niederhauser

J.S.D.C., **74**, 133–139 (March 1958)

A new method of dyeing polyacrylonitrile fibres at high temperatures, in the presence of hydroxylamine sulphate, is described in detail. The hydroxylamine salt seems to modify the nitrile groups into new functions containing amino groups, which confer on the fibre affinity for soluble and insoluble dyes of different classes— acid, direct, metal-complex, phthalocyanine, etc.
   AUTHORS

Dyeing of Acrylic Fibres, with particular reference to the Pack-dyeing of Courtelle
K. Meldrum and J. S. Ward

J.S.D.C., **74**, 140–150 (March 1958)

The general features of the dyeing behaviour and thermoplastic properties of acrylic fibres are discussed in relation to practical dyeing operations, in particular the pack- and package-dyeing of Courtelle in the form of loose fibre and slubbing. General and specific procedures for the application of disperse and basic dyes, consistent with the retention of good condition of the material, are suggested.   AUTHORS

Union Dyeing of Acrilan–Wool Blends
W. H. Hindle

J.S.D.C., **74**, 151–157 (March 1958)

Early methods of dyeing Acrilan–wool blends in solid shades are outlined and the limitations stated. A new method is described which is applicable to all classes of wool dyes. Data are presented to show how the concentrations of sulphuric acid and of a cation-active dyeing assistant may be varied to control the relative dyeing rates of wool and of Acrilan and the migration of dye from wool to the Acrilan acrylic fibre to produce solid shades.
   AUTHOR

Dyeing of Acrilan and Wool–Acrilan Blends
G. H. Lister

J.S.D.C., **74**, 158–163 (March 1958)

The acid-combining capacity of Acrilan has been determined using sulphuric acid at 60°c. The influence of pH on the dyeing of Acrilan with acid dyes has been examined, and the conditions required to obtain complete fibre penetration have been determined. The effect on the wool component of the blend and on the wearing properties of the cloths of the low pH required to dye Acrilan–wool blends satisfactorily with acid dyes has been investigated. The practical problems associated with the application of acid and chrome dyes in strongly acid dyebaths are discussed, and a dyeing method for their application is suggested.   AUTHOR

Electrochemical Surface Decoration of Aluminium Articles
P. V. Shchigolev

J. Appl. Chem. U.S.S.R., **30**, 882–887 (June 1957)

Conditions are described for electrolytically polishing and anodising aluminium. Anodising at a higher temp. and for a longer time produces a more absorbent oxide film, but the product is of inferior brightness. Similar results are obtained when A.C. is used. The anodised Al can be coloured by the incorporation of metallic precipitates in the pores of the oxide film, or by the formation of coloured lakes with conventional mordant dyes. The inorganic salts of Fe, Cu, Ag, Au, Pb, Co, etc. give blue and various brown and black effects. Treatment of the anodised Al with 1 g. of Mordant Yellow and 0·14–0·3 g. of Alizarine Red 8 in 1000 ml. of H_2O at 70–80°c. for 3–10 min. colours it gold. Similarly, yellows can be produced with Tartrazine, Chrysophenine, dibromofluorescein; blues with Aniline Pure Blue and Patent Blue; red with Bengal Red, fuchsine, and Rhodamine; and green with Naphthalene Green and Emeraldine.
   T.Z.W.

PATENTS

Dyeing Organic Derivatives of Cellulose blue with Azoic Dyes
Celanese Corpn. of America   *USP* 2,754,171

Good blues are obtained on cellulose acetate with azoic dyes if during formation of the dyes on the fibre there are present certain non-ionic surface-active agents, i.e. Atrosol C, Cerfak N-100, Softol 205 or Atlac G1020. Thus acetate rayon fabric is treated for 1 hr. at 75°c. in a bath containing 2% (on wt. of fabric) of 4-benzoylamino-2-5-diethoxy-aniline and 3% of β-hydroxynaphthoic acid o-toluidide. It is then diazotised, rinsed and treated for 60 min. at 75°c. in aqueous 1% soap containing 1·5% (by vol.) of Atrosol C. The product is a clear blue.   C.O.C.

Treating Aminoalkylated Cellulosic Textiles with 8-Hydroxyquinoline Sulphonic Acids and Metals Forming Chelate Rings
U.S. Secretary of Agriculture   *USP* 2,753,240

Aminoalkylated cellulosic textiles, e.g. those produced according to *USP* 2,459,222, are treated with an arylsulphonic acid containing chelate groups dissolved in a

dilute aqueous weak acid, until sulphonic acid salts of the amino groups in the fibres are produced. Fluorescent textiles are produced by further treating with metals that fluoresce when chelated, if copper is used then the product is also rot-resistant. Thus an aminoalkylated cellulosic textile was treated for 15 min. at 70°c. in aqueous 1% 8-hydroxyquinoline-5-sulphonic acid and 0·5% acetic acid and then for 2 min. in aqueous 0·5% acetic acid and 5% Cu acetate at 70–75°c. The product had good affinity for acid dyes. In ordinary light it was light green and in ultraviolet radiation it fluoresced to a deep wine red.

C.O.C.

Dyeing Acrylic Fibres
Deering Milliken Research Corpn.   *USP* 2,779,726

Acrylic fibres are readily dyed with acid dyes in presence of a cupric salt if an A.C. current is passed through the bath before dyeing commences. Thus a bath was made up of water (500 ml.). Roracyl Dark Green B (DuP) (1 g.), Anthraquinone Blue SWF 150% (DuP) (C.I. Acid Blue 25) (0·2 g.), Du Pont Orange RO (C.I. Acid Orange 8) (0·1 g.) and CuSO₄ (3 g.). The bath was brought to the boil and two copper electrodes each of 10 sq.in. were put in the bath. A 60 cycle A.C. (10 amp.) current was passed between the electrodes for 10 min. while the bath was boiling. The electrodes were then removed. Scoured Orlon yarn was then dyed in the boiling bath for 5 min. The dyed yarn was black, well penetrated and fast to repeated washings.

C.O.C.

Dyeing of Polyesters with Anthraquinone Disperse Dyes (IV p. 436)
Dyed Flame-resistant Fabric (X p. 443)

IX— PRINTING

Protection of Photographic Colour Images from Fading
Y. Tomoda and M. Kawasaki
Rept. Govt. Chem. Ind. Research Inst. Tokyo,
52, 364–367 (xliv) (Oct. 1957)

Two methods of protecting images produced by colour development were studied— (1) coating with an ultra-violet-absorbing substance such as quercetin (3:5:7:3′:4′-pentahydroxyflavone) and (2) use of antioxidants. Fading tests were made in a Fade-Ometer, with 6 hr. exposure for the yellow and magenta dyes and 12 hr. for the cyan dye. Fading was somewhat reduced by quercetin coating, but the results were not satisfactory. Treatment of colour-developed paper with antioxidants was more successful, especially when test pieces were immersed in a 1–3% solution of catechol. C.J.W.H.

PATENTS

Printing Paste
FBy   *USP* 2,779,686

Soluble or fusible substances containing both basic N groups capable of salt formation and groups which can cross-link with these N groups are used. Thus a basic polyurea of viscosity number *z*μ = 138 (prepared from 0·2 mol. of diethylene triamine, 0·8 mol. of γγ′-diamino-dipropylmethylamine and 1·0 mol. of tetramethylene di*iso*cyanate) is used in the following paste: for printing cotton or viscose rayon fabrics, 10% acetic acid solution of the polyurea (400 parts), 15% paste of copper phthalocyanine (C.I. Pigment Blue 15) (150), and water (550). The prints are heated at 100°c. for 5 min. and are then highly resistant to light and washing. C.O.C.

Printing Stripes on Fabric
Rock Hill Printing & Finishing Co.   *USP* 2,754,796

Colour is supplied to the surface of the printing roller which is doctored at regular intervals along its length before it contacts the fabric. This results in production of a differential striping of the fabric. The doctoring of the printing roller displaces or "ploughs" the doctored colour transversely, so that excess of colour concentrates at the edges of the striping causing the stripes to have heavy borders. C.O.C.

Photochemical Multicolour Printing of Textiles or the Like
Brown–Allen Chemicals   *USP* 2,756,144

A photosensitive diazonium salt and a photosensitised ester of a leuco vat dye are applied in solution to an area of the base. Part of this area is then irradiated in presence

of water to decompose the diazonium salt and precipitate the vat dye in the exposed part. The undecomposed diazonium salt is then treated with a coupling agent to form an azo dye and the remaining ester of the leuco vat dye washed out. Thus tetrabromoindigo dissolved in acetone is mixed with an aqueous solution of stabilised diazotised *p*-nitro-*o*-anisidine and then with aqueous urea and a sensitising solution containing uranium acetate. The acetone must form 50% of the final solution to prevent premature precipitation of the dye. Cotton cloth is treated with this solution and exposed to light through a screen. The exposed portions become blue. The cloth is then exposed to warm moist air containing ammonia vapour when the unexposed portions become red. If a negative is used instead of a screen then depending upon the depth of the various portions of the negative the resultant pattern obtained on the cloth may vary from red through purple to blue. C.O.C.

Xerographic Developer
Haloid Co.   *USP* 2,753,308

A xerographic toner composition comprises pigmented resin of particle size < 20 μ. The resin is a tough low-melting resin of polyvinyl-butyral blended with a thermoplastic formaldehyde type resin. Enough pigment should be used to cause the toner to be highly coloured so that it forms a clearly visible image on application. C.O.C.
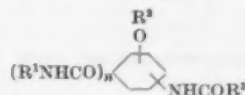
Mordanting Basic Dyes in Photography
Eastman Kodak Co.   *USP* 2,756,149

Compounds of formula—

$$(R^1NHCO)_n \overset{\overset{\displaystyle R^2}{\overset{\displaystyle O}{|}}}{\diamondsuit} NHCOR^3$$

(*n* = 0 or 1; R¹ and R² = monocyclic aryl groups of the benzene series, one or both of which contains one or more alkyl groups of > 3 C; R³ = monocyclic sulphoaryl or carboxyaryl of the benzene series), e.g. 5-[4-(2:4-di-*tert.*-amylphenoxy)-3-(phenylcarbamyl)phenylcarbamyl]-1:3-benzenedisulphonyl chloride, when used as mordants for basic dyes, greatly improve the stability of the dyes in organic colloid layers, e.g. gelatin, polyvinylchloride, hydrolysed cellulose esters, etc. They do not interfere with the bleaching properties of the dyes in photographic processes. C.O.C.

Reduction of Dye Stain in Processed Photographic Papers containing Dyes
Eastman Kodak Co.   *USP* 2,756,151

Addition of aryl or alkaryl sulphonic acids or sulphonates to the stop or fixing bath when processing photographic paper containing sensitising dyes, e.g. use of 0·5% sodium anthraquinone-β-sulphonate in an acid stop bath, almost completely eliminates dye stain. C.O.C.

Stabilised Colouring Compositions for Carbon Copying Hectographs, etc.; Manufacture and Use (IV p. 436)
Remazol (FH) Reactive Dyes (VIII p. 440)

X— SIZING AND FINISHING

Influence of Ion Exchange on Size and Shape of Chain-like Polyelectrolyte Molecules
R. E. Cooper and A. Wassermann
Nature, **180**, 1072 (16 Nov. 1957)

Addition of magnesium salts to sodium alginate gels causes an increase in mol. wt., thought to be due to inter-molecular salt links; and a decrease in viscosity, thought to be due to intramolecular salt links producing a more compact configuration. A.J.

Examination of some Factors in Cotton Sizing by means of Sized Rovings
M. Zilahi and I. Kelen
Magyar Textiltechnika, (10), 366–370 (1956):
Hungarian Tech. Abs., **9**, (4), 121 (1957)

The breaking strength of rovings is increased several thousands % by sizing; therefore the effect of sizing is more clearly visible than on sized yarn. The roving was fastened to a warp yarn on a Sucker TDC 11 machine before entering the size box. Tests established three important facts— (1) Higher starch concentration results

in increased size retention, higher breaking strength, and greater resistance to abrasion under otherwise identical conditions. (2) On raising the temperature from 58° to 99°c. at a given concentration, size retention shows a maximum at about 58°c. and at 85–90°c. Size retention occurs at the lower peak only on the surface, whereas the size penetrates between the fibres at the higher range and thus may be denoted as useful retention. Breaking strength and resistance to abrasion are considerably higher in the latter case. (3) Breaking strength and resistance to abrasion can be substantially increased by repeated sizing followed each time by drying.   C.J.W.H.

Milling of Wool and of other Animal Hairs
H. Zukriegel

Melliand Textilber., **39**, 85–88 (Jan. 1958)

Theoretical aspects of the milling of wool and of other animal fibres are reviewed with reference to the morphological and elastic properties of the fibres and the effect of milling assistants.   L.A.T.

Toxicity of Lithium Salts to Keratin-digesting Insect Larvae
J. R. McPhee

Nature, **180**, 1001–1002 (9 Nov. 1957)

Since cations are converted to sulphides by clothes-moth larvae, those which form insol. sulphides are detoxified, but those forming sol. sulphides stable at pH 10 may be toxic; e.g. lithium salts are toxic. Cations whose sulphides are unstable at pH 10 may be toxic if the hydroxides are sol., e.g. salts of barium and strontium. Tests with metals which form insol. sulphides, e.g. Fe, Hg, Sb, Ag, Cd, Pb, Cu, Ni, and Co, show them to be only slightly toxic, as are those which form unstable sulphides and insol. hydroxides, e.g. Al, Cr, Mg, and Ca.   A.J.

Behaviour of Resin-treated Fabrics towards Hypochlorite Solutions
R. Aenishänslin

S.V.F. Fachorgan, **13**, 5–9 (Jan. 1958)

Nitrogen-containing resins of the carbamide, melamine, and iminazole types are attacked by solutions of sodium hypochlorite and bleaching powder. The formation of chloramines also takes place. These are liable to decompose during subsequent heat treatments, giving rise to acidity, which leads to fabric tendering. Epoxy resins and ketone–aldehyde condensates are unaffected by hypochlorites.   L.A.T.

New Silicone Emulsions for Textiles
H. Enders and H. Neuwirth

Melliand Textilber., **39**, 80–85 (Jan.); 190–196 (Feb.); 309–319 (March 1958)

The chemistry of carbon and silicon is compared and contrasted. The development of stable silicone emulsions is described. Their properties and methods of application, and the types of finish produced, are discussed.

     L.A.T.

Water-repellent Finishes
H. Hilscher

S.V.F. Fachorgan, **13**, 27–31 (Jan. 1958)

A brief historical survey of water-repellent finishes on textiles is followed by a critical review of present-day methods. Reference is made to treatments which impart to fabrics resistance to soiling and water-borne stains. Methods of testing proofing effectiveness are mentioned.

     L.A.T.

Durability of Water-repellent Finishing
I. Králik and I. Gál

Magyar Textiltechnika, (9), 328–329; (10), 385–386 (1956): *Hungarian Tech. Abs.*, **9**, (4), 120 (1957)

In the theoretical examinations of Fobit, a Hungarian water-repellent agent, the capillary activity of textiles was computed at a 180° contact angle based on the most unfavourable case, i.e. on the max. pore diameter established by photoplanimetry. The computed capillary depression agreed well with the static water column pressure measured on the textiles made water-repellent. Fobit is stearamidomethylpyridinium chloride. Molten stearic acid and ammonia gas yield stearamide, and pyridine hydrochloride is obtained by the absorption of hydrochloric acid gas in pyridine. Whereas similar foreign materials are used in concn. of 15–20 g./litre, Fobit gives excellent results at 5–10 g./litre. Fobit already condenses at 90°c. The water column pressure values and the

sprinkle test values did not deteriorate either after ten household washings or after as many dry cleanings. The impregnation cannot be washed out because it forms compounds both with cellulose-base and with protein-base fibres.   C.J.W.H.

Application of Novel Chemical Compounds in the Finishing of Cellulosic Fabrics
W. Rümens

S.V.F. Fachorgan, **13**, 10–26 (Jan. 1958)

Recent developments in the field of "minimum-iron" finishes on cellulosic fibres are discussed. Particulars are given of an investigation of resins of the "reactive" type, including hydroxymethyl derivatives of ethyleneurea, hydroxyethyleneurea, and acetylenediurea. The treated fabrics were tested for crease recovery, tear strength, resistance to abrasion, residual shrinkage, and nitrogen content. Fabrics treated with these compounds have excellent fastness to washing. Combination of the resin with cellulose by means of direct cross-linking is postulated. The exact reaction mechanism has not yet been found.   L.A.T.

Kinetics of the Reaction between Amides and Formaldehyde
J. Ugelstad and J. de Jonge

Rec. Trav. chim., **76**, 919–945 (Nov. 1957)

Measurements of the rates of reaction of formaldehyde with benzamide, propionamide, and chloroacetamide, and of the rates of hydrolysis of the resulting hydroxymethylamides, show that formation of the hydroxymethylamide is a bimolecular reaction and its decomposition a unimolecular reaction. The reactions are catalysed by H_3O^+ and by OH^- and show general acid catalysis but not general base catalysis (except for the urea–formaldehyde system).   A.J.

PATENTS

Reducing the Tendency of Grafted Acrylonitrile Polymers to Discolour when treated with Alkali
ICI   *BP* 791,765

Grafted acrylonitrile polymers are given a cotton-like resistance to alkalis by treating them with an acid solution of an aldehyde. Thus a grafted acrylonitrile polymer yarn containing 15% water-soluble polyvinyl alcohol as the second component was treated with a solution of HCHO (7 parts), H_2SO_4 (10) and water (83) at 83°c. for 30 min. The treated yarn did not discolour when boiled for 5 min. in 1% aq. Na_2CO_3.   C.O.C.

Durable or Stiffened, Crease-resistant Finish
Monsanto   *USP* 2,755,198

Use of a water-soluble methylolimidazolidone-2, a water-soluble polymeric material containing several carboxyl or carboxylanhydride groups, e.g. a water-soluble vinyl acetate-maleic anhydride copolymer, and a water-soluble polyhydric compound containing > 1 hydroxyl group, e.g. polyvinyl alcohol, yields a finish which is firmer and more durable than that obtained by use of a polymethylol melamine or dimethylol urea. In addition it is more resistant to chlorine pick-up and is better able to recover from creasing.   C.O.C.

Dyed Flame-resistant Fabric
Johns–Manville Corpn.   *USP* 2,755,534

A strong, lightweight, woven asbestos fabric containing $> 25\%$ cellulosic reinforcing fibres is treated with an inorganic flame-resisting finishing agent together with a thermoplastic resin containing chlorine, e.g. a mixture of diammonium hydrogen phosphate, antimony trioxide, urea (buffer for cotton content) and a 90 : 10 polyvinyl-chloride–vinyl acetate copolymer. The treated fabric dyes level with vat dyes. Alternatively the yarn may be treated and dyed before being woven into fabric. C.O.C.

Coating Textiles and other Materials with Perfluorochloroolefin Polymer
M. W. Kellog Co.   *BP* 791,092

Epoxide resins are excellent agents for bonding textiles and other materials to perfluorochloro-olefin polymer.   C.O.C.

Coating of Nylon Fabric
United States Rubber Co.   *BP* 791,618

Successive treatments of nylon fabric with a polyester-diisocyanate precondensate and a catalyst rapidly and efficiently produces a fabric that is coated with a rubbery

polyurethane. The coated fabric is porous and is very hard wearing when used for shoe uppers.   C.O.C.

Relationship between Constitution and Activity of Antistatic Agents (III p. 429)

Action of N-Ethylmaleimide on Wool and its use for the Estimation of Thiol Groups (XIV p. 448)

XI— PAPER AND OTHER CELLULOSIC PRODUCTS

Preparation of Paper from Synthetic Fibres
K. Klein

S.V.F. Fachorgan, 13, 61–64 (Feb. 1958)

Some technological aspects of the manufacture of paper from synthetic fibres are described. An account is given of the physical properties of these papers and reference is made to their application.   L.A.T.

Behaviour of Various Dyes towards Deinking Chemicals
R. W. Kumler

Paper Industry, 39, 916–917 (Feb. 1958)

A quick reference guide showing the colour fastness of dyes to alkalis, hypochlorite, peroxide, and hydrosulphite. The dyes examined are referred to by class and *Colour Index* number. The data given in a table are based on spot tests given by dye manufacturers.   R.A.

"Limiting" Degree of Polymerisation of Cellulose
V. I. Sharkov, I. I. Korol'kov, and E. N. Garmanova

J. Appl. Chem. U.S.S.R., 30, 1668–1672 (Nov. 1957)

The "limiting hydrolysability" of cellulose depends upon its micro-structure and the composition of the reaction medium. The reactivity of the medium is inversely proportional to the mol.wt. of the alcohol used. The stretching of the regenerated cellulose in the coagulating bath lowers the limit of hydrolysis and increases the easily hydrolysable amorphous fraction, whilst swelling produces the opposite effect.   T.Z.W.

Liberation of Carboxyl Groups in Cellulose
O. Ant-Wourinen and A. Visapää

Svensk Papperstidning, 61, 27–33 (31 Jan. 1958)

The findings of Franzon and Samuelson (*ibid.*, 60, 706 (1957)), that HCl used for liberating the carboxyl groups is easily washed out of the fibres, are challenged. The amounts of distilled water remaining attached to 10 mg. of cotton cellulose, sulphite pulp, and rayon have been measured, and the maximum removal of impurity calculated on the basis of the dilution occurring at various stages of washing. Franzon's radioactive tracer method is not considered sufficiently accurate. Eleven washing tests, using three grades of distilled water, showed that complete carboxyl liberation can be achieved only by using pure water saturated with CO_2.

O. Samuelson

Ibid., 33–34

The above criticism is based on a calculation which does not take into account the fact that the electrolytic concentration inside a cellulose fibre is lower than in the external solution. Franzon and Samuelson used water that had been both deionised and distilled, so that there was no question of contaminants affecting results, as suggested. When distilled water purified by ion-exchange is used, there is no risk of adsorption of cations from the water.   R.A.

Chemistry of Xanthates and of Viscose. VI— Interdependence of Components of Viscose
S. N. Danilov and N. F. Gintse

J. Gen. Chem. U.S.S.R., 27, 3290–3301 (Dec. 1957)

The effect of pH upon the rate of decomposition of cellulose xanthate in aqueous media, in absence and presence of salt or sodium sulphide, is studied; the lower the pH the nearer the rate of decomposition approaches that in water. Effects of the addition of salts, and of the nature of the salt, upon the stability to gelation is studied. An explanation of the presence of sodium sulphide as a primary decomposition product of cellulose xanthate is given in terms of the trithiocarbonate, since on ageing the concn. of Na_2S decreases, whereas that of trithiocarbonate increases.   G.J.K.

Stabilisation of Cellulose towards Alkaline Degradation
G. Machell and G. N. Richards

Tappi, 41, 12–16 (Jan. 1958)

The degradation of cellulose by boiling dilute sodium hydroxide is decreased by modification of the reducing end-group (e.g. by glucoside formation) or by suitable variation of the three relative rates of the "degradation" and "stopping" reactions. Applications of either type of procedure to hot-alkali pulp refining reduces the efficiency of hemicellulose extraction by non-swelling alkali.   R.A.

Attack of Molecular Oxygen on Alkali Cellulose
H. G. Müller

Textil-Rund., 12, 622–635 (Nov.);
671–684 (Dec. 1957); 13, 67–81 (Feb. 1958)

The influence of oxygen on the alkali and water absorption and the attendant swelling was studied on carefully purified cotton and to a less extent on viscose rayon using cuprammonium fluidities as the measure of attack. Although the relation of the sodium hydroxide absorption *a* of native, mercerised, and reprecipitated cellulose to the alkali concentration *c* is irregular, and the water absorption *w* in all three cases shows a maximum, within limits a linear relation obtains—

$$\frac{a}{w} = kc$$

    S.R.C.

## Interaction of some Organo-silicon Compounds with Cellulose Nitrates
A. P. Kreshkov, I. Ya. Guretskii, and P. A. Andreev

J. Gen. Chem. U.S.S.R., 28, 187–193 (Jan. 1958)

The reaction between cellulose nitrate and various di- and tetra-alkoxysilanes is studied, and the heats of swelling and the infrared spectra in the 3-μ. region (O–H stretching frequency region) of the products of the reaction are determined. Fundamentally, condensation occurs through the free OH groups with the elimination of alcohol—
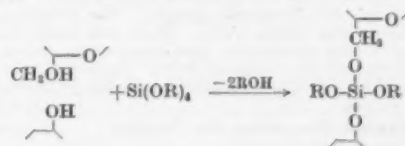
On the other hand, under certain conditions elimination of nitrous oxides occurs simultaneously, and on this evidence the authors postulate a side-reaction as follows—
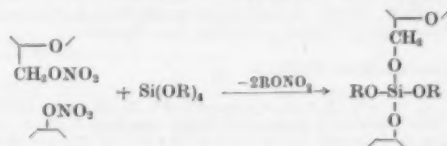
    G.J.K.

Distribution of Substituents in Partially Methylated Celluloses. II— Methylcelluloses prepared from Sodium Cupricellulose
I. Croon, B. Lindberg, and A. Ros

Svensk Papperstidning, 61, 35–37 (31 Jan. 1958)

Methylation occurs at first mainly at C^2 and C^3. A cyclic structure for sodium cupricellulose is proposed with the metal linked to the oxygen atoms at C^2 and C^3, the remaining Cu valencies either bonded to two hydroxyls or involved in cyclic complex-formation with another glucose residue. Once an oxygen at C^2 or C^3 is methylated, the complex collapses, and the reactivities of the remaining hydroxyl groups towards methylation increase.   R.A.

Carboxymethylcellulose. IV— Optical Investigations
J. Schurz and E. Kienzl

Mh. Chem., 88, (6), 1017–1023 (1957)

Whereas ultraviolet and infrared spectrographic data do not indicate the presence of any other substance of a chemical character, X-ray examination revealed that crystallites of cellulose II occur between the planes of the glucose rings and are probably bound there by subsidiary

valences. This crystallite material has been identified with certain "gel bodies" observed in solutions.

H.H.H.

Dimethyl Sulphoxide as a Solvent for Cellulose Ethers
R. St. Manley

Svensk Papperstidning, **61**, 96–98 (28 Feb. 1958)

Dimethyl sulphoxide is a good solvent for non-ionic cellulose ethers and the only known organic solvent for water-soluble ethyl-hydroxyethyl-cellulose, possessing certain advantages over water for viscosity measurements. For certain measurements, e.g. ultra-centrifugation, its high viscosity, high refractive index, and hygroscopicity may give rise to difficulties. Experimental results are given for methyl-, hydroxyethyl-, methyl-hydroxyethyl-, and carboxymethyl-cellulose.   R.A.

PATENT

Flame-resistant Regenerated Cellulose Film
American Cyanamid Co.   *USP* 2,757,102

The film, either when wet and swollen during manufacture or dry, is treated with diammonium phosphate and dicyandiamide dissolved in an aqueous polyhydric alcohol. The treated film is clear, sparkling, shows no signs of crystalline deposit and has good flame-resistant properties.   C.O.C.

Stabilised Colouring Compositions for Carbon Copying Hectographs, etc.; Manufacture and Use (IV p. 436)

XII— LEATHER; FURS; OTHER PROTEIN MATERIALS

Inorganic Pigments for Colouring Leather
A. L. Zaides and R. A. Metlitskaya

J. Appl. Chem., U.S.S.R., **30**, 1633–1641 (Nov. 1957)

Electron-microscopic study of Fe oxide, TiO_2, and Pb pigments show that the quality of their thin films on leather depends on the form, uniformity, and particle size of the pigments.   T.Z.W.

Waterproofing of Leather with Organo-silicon Compounds— IV
E. K. Meminov and M. G. Voronkov

J. Appl. Chem. U.S.S.R., **30**, 974–976 (June 1957)

Leather is made waterproof by the application of a 5% soln. of diacetoxymethylstearoxysilicon $(O \cdot CO \cdot CH_3)_2 \cdot O \cdot CO \cdot C_{17}H_{35}$ in toluene containing 0·01% ethyl orthotitanate as catalyst, drying in the air for 1–3 hr. and at 60–70°c. for 5–6 hr. Somewhat inferior results are obtained by immersion of leather in a 0·5–1% aq. soln. of $C_2H_5 \cdot Si(OH)_2 \cdot ONa$ containing 1·25% of a plasticiser.   T.Z.W.

Action of Acrylonitrile and Acrylamide upon Collagen
L. Seligsberger and H. Clayton

J. Amer. Leather Chem. Assocn., **53**, 90–102 (Feb. 1958)

Acrylonitrile and acrylamide react with limed hide in strongly alkaline soln. Up to 1·4 millimoles per gram of collagen have been introduced into the collagen mol. Though the fixation of these monomers results in a lowering of the shrinkage temp. and in a decreased Cr fixation, the dry fibre strength of the resulting leather is not materially affected. The ε-amino groups of the collagen are believed to be the active sites in the cyano- and carbamoyl-ethylation reactions.   J.W.D.

Wettability of Chrome-tanned Leather
R. G. Mitton and C. D. Pomeroy

J. Soc. Leather Trades Chem., **41**, 402–417 (Dec. 1957)

Wettable leather with high chrome contents may be made by degreasing the pelt thoroughly before tannage; it becomes water-repellent during storage, presumably owing to the formation of more basic chrome complexes. The change is accelerated by heat and, if the leather is thoroughly dry, acid escapes from the surface of the leather leaving a highly water-repellent film not more than 1 mm. thick; the leather inside, from which acid cannot escape, remains easily wettable. If the leather contains even small quantities of fatty acid, chrome soaps are formed during tannage, and the leather is water-repellent throughout. Changes in the chrome complexes are probably associated also with changes of feel which occur during ageing or intensive drying; studies of the rates at which fat-free leather develops water-repellency have thus

a further interest. The results of some experiments on these lines are reported.   J.W.D.

Review of Work on the Effect of Nitrous Acid on Collagen
A. Küntzel

Leder, **8**, 34 (1957):
J. Soc. Leather Trades Chem., **42**, 62 (Feb. 1958)

Nitrous acid, formed by the reaction of sodium nitrite with sulphuric or acetic acid, acts differently on various amino acids in collagen without influencing its structure. Mostly affected are lysine (deamination), arginine (change of guanidino into cyanamido group), and tyrosine (introduction of nitroso, nitro, and diazo groups). Serine and threonine are affected to only a slight extent. In contradiction to reports of several workers, it is found that nitrous acid exerts no tanning effect on collagen. If nitrous acid is formed within the fibre, opening up of the structure occurs.   C.J.W.H.
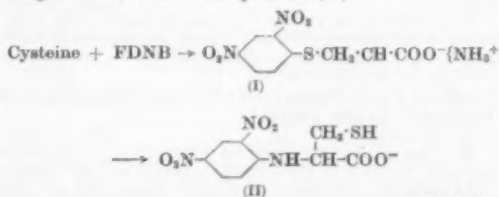
Molecular Rearrangement in the Reaction of Cysteine with 1-Fluoro-2:4-dinitrobenzene
H. P. Burchfield

Nature, **181**, 49–50 (4 Jan. 1958)

Reaction velocity, light-absorption measurements, and other tests suggest that alkylation of the thiol group occurs to give I, and this is followed by a rearrangement to give an N-substituted product (II)—

Cysteine $+$ FDNB $\rightarrow$ O_2N⟨⟩$S \cdot CH_2 \cdot CH \cdot COO^- (NH_3^+$

(I)

$\longrightarrow$ O_2N⟨⟩$NH \cdot CH \cdot COO^-$ with NO_2 and $CH_2 \cdot SH$

(II)

W.R.M.

Halogenoarylation of Unsaturated Compounds with the aid of Aromatic Diazo Compounds. X— Synthesis of DL-Phenylalanine and its Homologues
A. M. Yurkevich, A. V. Dombrovskii, and A. P. Terent'ev

J. Gen. Chem. U.S.S.R., **28**, 227–230 (Jan. 1958)

Arachin Molecule
C. W. Cater, W. E. F. Naismith, R. H. K. Thomson, and G. R. Ure

Nature, **180**, 971–973 (9 Nov. 1957)

Work is reviewed on the denaturation of arachin, particularly by the action of guanidine hydrochloride, by urea, and by varying ionic strength. The view is expressed that the complete globular arachin molecule is composed of two half-molecules, probably held together by salt links. These in turn are bundles of about five sub-units of folded polypeptide chains held together by hydrogen bonds. Dissociation to the separate sub-units occurs without the breakdown of peptide bonds, and no new terminal groups are formed. The sub-units are all liberated simultaneously and become free to unfold at the same time. Fibres cannot be formed before this stage.   A.J.

PATENT

Making Leather Water-repellent
Boehme Fettchemie   *BP* 791,633

Leather is treated with an organic metal complex obtained by treating a basic salt of a polyvalent metal with a derivative of an acid of bascity > 2, this derivative containing a high-mol.wt. aliphatic, cycloaliphatic, aliphatic-aromatic or aliphatic-cycloaliphatic residue. Thus chrome tanned and neutralised cowhides are treated at 50°c. with an aqueous solution of the ammonium salt of an acid dodecylphosphate. The leather is then coloured as usual, and fat-liquored.   C.O.C.

XIII— RUBBER; RESINS; PLASTICS

Block and Graft Polymers
M. L. Miller

I— Graft Polymers from Acrylamide and Acrylonitrile

Canadian J. Chem., **36**, 303–308 (Feb. 1958)

Graft polymers of acrylonitrile and acrylamide with 1–20 grafts have been prepared by chain transfer to polymer and by photolysis of a polymer containing a few

% of α-chloroacrylonitrile. Intrinsic viscosities and softening points are found to depend on the number of grafts.

II— Block Polymers from Acrylamide and Acrylonitrile and from Acrylamide and Acrylic Acid

ibid., 309–314

Block polymers have been prepared by photolysis of polymers with end-groups containing bromine. Intrinsic viscosities and softening points are compared with those for random copolymers of the same composition and molecular weight. W.R.M.

Preparation and Properties of Trimers of Alkyl Acrylates and Alkyl Methacrylates
A. Ya. Drinberg and A. D. Yakovlev

J. Appl. Chem. U.S.S.R., 30, 1204–1214 (Aug. 1957)

Linear polymers of *n*-alkyl acrylates and methacrylates can be converted into insoluble trimers by heating their films in air at 160–200°c. The relative ease of change is directly proportional to the length of the alkyl chain (1–8 C) and the D.P. The polymers of acrylic acid are more easily converted than the corresponding derivatives of methacrylic acid. The ring closure is the result of the increase in the number of polar groups. T.Z.W.

Coating Rubber
ICI BP 791,280

The adhesion to rubber of lacquers based upon polyesters or polyesteramides and organic isocyanates is much improved if the rubber is first treated with an aqueous halogen or sulphuric acid. C.O.C.

White or Pastel Pigmented Vinylidene Copolymer of Improved Colour Fastness
Dow Chemical Co. USP 2,753,321

Moulded or extruded articles made from a vinylidene chloride polymer or copolymer, a plasticiser, an organic light stabiliser, e.g. salol, an alkaline phosphate or other basic stabiliser, a white or light coloured pigment, and as colour stabiliser, an aliphatic di- or tri-carboxylic acid and/or anhydride and/or alkali metal salts of such acids, there being 0–2 hydroxyl groups in the acid chain but no other functional substituent, have good initial colour which does not deteriorate on long storage. Suitable colour stabilisers are sebacic, aconitic, fumaric, tartaric and malonic acids, chloromaleic, maleic or di*iso*butenyl succinic anhydrides; a mixture of citric acid and maleic anhydride, or oxalic acid and sodium oxalate, or sodium oxalate and maleic anhydride. C.O.C.

Dispersion of Perfluorochlorocarbon Polymers
M. W. Kellogg Co. BP 791,263

Resinous polymers of trifluorochloroethylene containing 0–15 mol. % of a comonomer copolymerisable with trifluorochloroethylene when dispersed in a solution of a copolymer of trifluorochloroethylene with a hydrogen-containing halogenated olefin have viscosity sufficient to enable them to be satisfactorily used for dip or flow coating. C.O.C.

Coatings and Mouldings from Polyglycidyl Ethers (V p. 439)

XIV— ANALYSIS; TESTING; APPARATUS

Precipitation of Magnesium with (Ethylenedinitrilo)-tetra-acetic acid
C. E. Bricker and G. H. Parker

Anal. Chem., 29, 1470–1474 (Oct. 1957)

Between the limits pH 3·5 and pH 4·0 magnesium is pptd. slowly and quant. by an excess of the sodium salt of (ethylenedinitrilo)tetra-acetic acid as $MgC_{10}H_{14}O_8N_2$, $6H_2O$. Properties and rate of pptn. of this magnesium salt are given. L.T.W.

Colorimetric Determination of Chromium in Sewage and Industrial Wastes
A. A. Christie, J. R. W. Kerr, G. Knowles, and G. F. Lowden

Analyst, 82, 336 (1957):
J. Soc. Leather Trades Chem., 42, 63 (Feb. 1958)

Organic matter is removed by oxidation with nitric and perchloric acids, and ignition; the residue is dissolved in hydrochloric acid. Ammonium persulphate and silver nitrate oxidise the chromium to dichromate, which gives a

red–violet colour with diphenylcarbazide. Chloride is first removed by evaporation to fuming with sulphuric acid. Permanganate, if formed from manganese compounds, is reduced with sodium nitrite. The colour with diphenylcarbazide is compared visually with standards, or the optical density is determined. C.J.W.H.

Semi-quantitative Estimation of Sodium Dithionite
T. P. Whaley and J. A. Gyan

Anal. Chem., 29, 1499 (Oct. 1957)

Sodium dithionite reacts with Naphthol Yellow S (C.I. Acid Yellow 1) to form a red colour which fades to yellow with increasing rapidity as the dithionite concn. increases. The dithionite concn. can be estimated from the time of fading. L.T.W.

Polarographic Investigation of Sodium Dithionite
F. Péter

Acta Chimica Academiae Scientiarum Hungaricae,
9, (1–4), 421–433 (1956):
Hungarian Tech. Abs., 9, (4), 108 (1957)

The polarographic behaviour of sodium dithionite was studied in order to determine the possibility of its quantitative determination by polarography. Sodium dithionite yields a readily evaluable anodic wave below 15–20°c. and in the pH range 7–14. At higher temp. (20–25°c.) a second anodic and a similarly high cathodic wave appeared. Further increase of temp. resulted in a parallel increase of the two latter waves, whereas the first anodic wave decreased. In the determination of sodium dithionite, the first wave is suitable for establishing the correlation between concentration and wave height. The presence of thiosulphate and sulphite does not affect the quantitative determination; there is an interfering action by sulphide, which, however, can be eliminated by adding zinc carbonate. C.J.W.H.

Analyses of Dye Intermediates by Improved Absorption Spectroscopy
N. Oi and K. Miyazaki

I— Quantitative Analyses of Chloronitrobenzene Isomers

Yakugaku Zasshi, 77, 1027–1029 (1957)

Determination of a mixture of 2- (I), 3- (II) and 4-nitro-1-chlorobenzene (III), difficult by the known method, was attempted by infrared absorption spectral measurements. Examination of the results by Youden's assay method (*Chem. Abs.*, 42, 2694 (1948)) showed the standard deviation was 0·63% with I, 0·60% with III and 0·33% with II.

II— Quantitative Analyses of Chlorodinitrobenzene Isomers

Ibid., 1030–1032:
Chem. Abs., 52, 985 (25 Jan. 1958)

A mixture of 2:4- (IV), 2:6- (V) and 3:4-dinitrochlorobenzene (VI) was similarly examined. The standard deviation was 0·56% for IV, 1·68% for V and 0·51% for VI. C.O.C.

Determination of Nitro Compounds with Titanium (III) Polyphosphate Solution— Application of Polyphosphate to Masking Volumetric Analysis
S. Suzuki, Y. Muramoto, M. Ueno, and T. Sugano

Bull. Chem. Soc. Japan, 30, 775–778 (Oct. 1957)

The nitro cpd. is reduced with an excess of standard Ti$^{\mathrm{III}}$ polyphosphate (I) soln. and back-titrated with potassium dichromate, Ce$^{\mathrm{IV}}$ sulphate, or sodium vanadate soln. Methylene Blue, diphenylamine, or Indigo carmine may be used as indicator; the choice varies with the cpd. under analysis. The high results given with dinitro cpd. by the method of Knecht and Hibbert (*Ber. deutsch. Chem. Ges.*, 36, 1549 (1903); 38, 3318 (1905); 40, 3819 (1907)) and reported by English (*Anal. Chem.*, 20, 745 (1948)) are not obtained with the method reported. Commercial picric acid cannot be analysed by this method, since its soln. containing I have a pronounced colour which masks that of the indicator. Trinitrotoluene gives only ca. 96% of the theoretical value. J.W.D.

Polarographic Investigations of the Organic Metal Complexes of Quinalizarin
E. Bodor

Acta Chimica Academiae Scientiarum Hungaricae,
9, (1–4), 375–380 (1956):
Hungarian Tech. Abs., 9, (4), 110 (1957)

Quinalizarin (1 : 2 : 5 : 8 - tetrahydroxyanthraquinone) proved to be reducible by polarography in basic solutions

at a pH value above 5·5. Its half-wave potential lies in an acetate buffer of pH 5·6 at − 0·6 v., in a 0·1 M. ammonium hydroxide–ammonium chloride solution at 0·75 v., and in a 0·1 M. sodium hydroxide solution at 0·9 v. referred to the saturated calomel electrode. Aluminium(III) ions had no effect on the quinalizarin wave in a strongly alkaline solution. Calcium and zinc ions, however, decreased the intensity of the diffusion current in proportion to the concentration of metal ions. A similar reduction of wave height occurred when aluminium ions were present in a basic solution of ammonium hydroxide–ammonium chloride.   C.J.W.H.

Determination of the Maturity of Raw Cotton by Differential Dyeing, Ribbon Width, and Micronaire Value
L. J. Rony

Bull. Inst. Text. France, (68), 31–52 (June 1957)

The method previously described (*ibid.*, (63), 15 (1956)) gives low values for the maturity of cottons of long staple and small ribbon width because the count of green fibres depends on the ribbon width, and this must be taken into consideration when the cumulated frequency curves for the fibres are constructed. The wall thickness at the limit of maturity is found to increase to a maximum at an average ribbon width of ca. 18·5 μ. The precision of the modified differential dyeing method is comparable with that of standard maturity, and the method gives a better indication of the distribution of fibre diameter in the sample.   J.C.F.

Reproducibility of Measurements of Degree of Polymerisation and of Swelling on Spun Viscose Rayon Staple
J. P. Fleury and M. T. Reitzer

Bull. Inst. Text. France, (68), 15–30 (June 1957)

An analysis of variance for the results of D.P. measurements on spun viscose rayon in cupriethylenediamine indicates that the main component of the variance arises in the viscosity determinations. For swelling measurements, the nature of the experimental errors precludes the determination of the separate contributions of sampling and of the measurements to the total variance. To detect a significant difference between the mean swelling values for two samples, the *t*-test should be applied.   J.C.F.

Determination of Sulphur and its Compounds in Rayon
M. J. Maurice

Text. Research J., **27**, 774–782 (Oct. 1957)

The compounds are sulphides, sulphites, xanthates, and sulphates. The methods for the determination of these compounds and of sulphur were first applied to standard soln. to establish that they yielded accurate results; then they were applied to the determinations in rayon. Apart from these determinations, the sums of some and of all compounds were found. These sums were found to be in good agreement with those calculated from the individual amounts, so it is assumed that all methods yield accurate results when applied to the determinations of the sulphur compounds in rayon.   S.B.D.

Direct Dye Staining of Viscose Rayon Cross-sections and some of its Applications
K. Kato

Text. Research J., **27**, 803–808 (Oct. 1957)

A differential staining method for the skin of viscose rayon is described. The procedure consists in dyeing fibre cross-sections with a blue direct dye, and then washing through the usual alcohol series. The results obtained are identical with those of the Victoria Blue method and are comparable to those of the Gentian Violet method. It is most probable that all these microscopical stains differentiate between the skin and the core in the normal viscose rayons only in terms of physical phenomena, such as diffusion, absorption, and swelling. The skin is stained much more slowly, but retains the dye much more strongly than the core, which is quickly dyed and readily washed out. The present technique has been applied to a wide range of cellulosic fibres, some of which are found to give results similar to the core, whilst others are similar to the skin in their staining properties.   S.B.D.

Determination of the Accessibility of Wool to Sorbates
J. H. Bradbury

Text. Research J., **27**, 829–831 (Oct. 1957)

Comment is made on the sorption isotherm method of measuring accessibility, and a method is suggested based on the measurement of the empty space within the fibre which is occupied by the sorbate at saturation regain.   S.B.D.

Action of N-Ethylmaleimide on Wool and its use for the Estimation of Thiol Groups
R. W. Burley and F. W. A. Horden

Text. Research J., **27**, 615–622 (Aug. 1957)

N-Ethylmaleimide in pH 3·5 aqueous buffer soln. combines slowly with Merino wool which is intact. It combines more rapidly after the wool has been super-contracted or pulverised, and equilibrium is apparently reached when an amount about 30% greater than the thiol-group concn. has reacted. The reasons for the higher value are not certain, but there does not appear to be reaction of N-ethylmaleimide with other groups. There is no appreciable discrepancy with copper-deficient wool, which has about four times as many thiol groups, and the agent may be used to estimate the groups in samples of this wool. Some of the physical properties of Merino wool containing a known amount of reacted N-ethylmaleimide are described.   S.B.D.

Evaluation of Soil Removal from Cotton Fabrics
W. J. Diamond and H. Levin

Text. Research J., **27**, 787–795 (Oct. 1957)

Certain characteristics of a soil–fibre complex are critically important to valid comparison of the relative soil-removal abilities of washing machines and detergents. The characteristics considered were obtained by a method of direct precipitation of zirconyl phosphate soil in cotton fabric. Soiled test cloths thus prepared permitted the evaluation of soil removal with a high degree of precision and reproducibility.   S.B.D.

Laboratory Micro-dyeing Apparatus
F. Péter and B. Mihalik

Textil Praxis, **12**, 478–479 (May 1957)

A self-contained micro-dyeing apparatus is described. The dye liquor is circulated continuously, and the direction of flow can be reversed. Redox potential, pH, and other measurements can be conveniently carried out at any stage of the dyeing process. The apparatus can also be used for the study of vat and sulphur dyes.   L.A.T.

Standard Methods for the Assessment of the Colour Fastness of Textiles (Third Report of the Fastness Tests Co-ordinating Committee)— First Supplement
Society of Dyers and Colourists

J.S.D.C., **74**, 22–37 (Jan. 1958)

Use of Fading Lamps
Institut Textile de France

Bull. Inst. Text. France, (70), 79–82 (Oct. 1957):
Teintex, **23**, 46 and 49 (Jan. 1958)

Authorised by the Commission d'Étude des Essais de Solidité des Teintures of the Institut Textile de France, recommendations are made on the choice of apparatus, the regulation of temperature and humidity, the mode of operation, and the evaluation of results.   S.R.C.

Quantitative Determination of Formaldehyde and Paraformaldehyde (Polyoxymethylene) in presence of one another
Z. Bellen

Chim. et Ind., **78**, (3 bis), 76 (Sept. 1957)

The direct determination of formaldehyde by the dimedone condensation is modified by precipitating the formaldimedone at pH 4·6, filtering off the precipitate, and titrating with caustic soda. Under these conditions there is no depolymerisation of the paraformaldehyde. The most accurate method for determining formaldehyde plus paraformaldehyde is that of Romijn: the alkaline solution is oxidised with iodine, and the excess of iodine back-titrated with thiosulphate.   C.J.W.H.

Estimation of Formaldehyde by Romijn's Method in the presence of Ammonium Salts
S. Bose

J. Indian Chem. Soc., **34**, 497–500 (July 1957)

The interference by ammonium salts in the estimation of formaldehyde by the hypoiodite oxidation method is

completely prevented by the addition of 3% mercuric chloride and 40% potassium iodide. The oxidant was shown to be sodium hypoiodite and not $K_3(HgI_4)$.

C.H.R.

Characterisation and Estimation of Condensation Resins on Cellulose Fibres
R. Aenishänslin

S.V.F. Fachorgan, 12, 602–612 (Sept. 1957)
Qualitative tests for CH_2O, urea, thiourea, cyclic ethyleneureas, and melamine are given. A quantitative method based on HCl-deresination, CH_2O, total N, and the formation of tetrachloromelamine is advanced. A reaction table of the more important resins is included.

S.R.C.

Method for studying the Deformation of Fabrics in Creasing
R. Steele

Text. Research J., 27, 695–700 (Sept. 1957)
A procedure has been devised for obtaining the load–deformation curve of a fabric during a deformation which begins as a small-radius bend and ends in crease formation. Curves obtained in this way on a variety of fabrics, including some resin-finished ones, indicate that the procedure should be of value in studying stiffness, resilience, crease-recovery, and other properties related to the drape and handle of fabrics.

S.B.D.

Automatic Ignition and Timing of the Flame in the Vertical Fire-resistance Test
J. D. Tallant

Text. Research J., 27, 825–826 (Oct. 1957)
An electrical method of lighting, timing, and extinguishing the flame is described. By eliminating the pilot light or the manipulating bar and controlling the gas flow automatically, the operator can give his whole attention to the flaming characteristics of the material under test.

S.B.D.

Comparative Infrared Spectroscopy of Commercial Polyamide Fibres
P. Bouriot

Bull. Inst. Text. France, (68), 7–13 (June 1957)
The polyamides 6,6-nylon, 6-nylon (Perlon), and 11-nylon (Rilsan) were deposited in thin films by evaporation of formic acid solutions. Although correlation exists between the position of the fundamental N–H band at 3 μ. and the hydrogen-bonded N–O distance in the three polyamides, conclusive identification relies on the spectrum above 8 μ., which is determined by the number of adjacent methylene groups.

J.C.F.

Determination of Total Oxidising Power of Buffered Chlorous Acid Solutions
Y. Tomimatsu and H. F. Launer

Anal. Chem., 29, 1500–1501 (Oct. 1957)
Two sensitive and precise procedures have been developed for the determination of the total oxidising power of buffered chlorous acid solutions which contain chlorate and chlorine dioxide. With either procedure the total oxidising power of acidified sodium chlorite solutions containing a total of 0·22 oxidising milliequiv. can be determined with a standard deviation of 0·13%. L.T.W.

Flame-photometric Determination of Calcium in Cellulose
L. H. Phfer

Anal. Chem., 29, 1528–1531 (Oct. 1957)
The cellulose sample is wet-ashed with H_2SO_4 and 30% H_2O_2, and after dilution the calcium is determined with a flame photometer, the emission at 422·7 mμ. · being measured. Other metal ions which may be present do not interfere. Comparative and recovery data for this method and the conventional volumetric oxalate method are given, and the accuracy and the precision of the two methods are discussed. L.T.W.

Determination of the Intrinsic Viscosity of Cellulose in Cupriethylenediamine
J. Cyrot

Bull. Inst. Text. France, (68), 55–66 (June 1957)
A simplified method for the preparation of cupriethylenediamine solution is described. A number of useful hints on the determination of the D.P.s of celluloses are given. J.C.F.

Polarographic Determination of the Methylene Blue Number of Regenerated Celluloses of High Carboxyl Content by the Suppression of Oxygen Maxima
I. Rusznák, I. Králik, and K. Fukker

Acta Chimica Academiae Scientiarum Hungaricae, 9, (1–4), 59–71 (1956):
Hungarian Tech. Abs., 9, (4), 112 (1957)
Detailed investigations were carried out to develop a well defined polarographic method of determining the methylene blue number in cellulose samples of high carboxyl content, and to establish the stoichiometric correlation between the methylene blue number obtained by means of polarography and the carboxyl content. A concentration of 0·004 M. and a liquor ratio of 6 : 1, applied so far, are unsatisfactory even for cellulose samples of medium carboxyl content, because of the insufficient amount of Methylene Blue (C.I. Basic Blue 9) present; therefore a concentration of 0·02 M. and a liquor ratio of 100 : 1 were introduced. Under these conditions the exact correlation could be established between the methylene blue number and the carboxyl content. The % carboxyl content of the sample is obtained by deducting the value of adsorption from the methylene blue number and then dividing the reduced methylene blue number by 7. With the suppression of oxygen maxima method, the concentration of the methylene blue solutions can be determined very accurately by polarography. The experiments were conducted on viscose rayon fibres oxidised with nitrogen dioxide. C.J.W.H.

Direct Colorimetric Determination of Cellulose Nitrate in Lacquers
M. H. Swann

Anal. Chem., 29, 1504–1505 (Oct. 1957)
The yellow colour formed by reaction of cellulose nitrate with alkali in presence of acetone provides a simple and rapid method for direct determination of cellulose nitrate in lacquers. L.T.W.

Determination of Cellulose Resins in Coatings by Colorimetric Cellulose Analysis
M. H. Swann

Anal. Chem., 29, 1505–1506 (Oct. 1957)
The intense blue–green colour formed by reaction of anthrone with cellulose in H_2SO_4 provides a method for the detection or determination of cellulose resins in coating materials without interference from plasticisers or other resins. Anthrone is a non-specific reagent used for carbohydrates in general, but in the field of coating resins the non-specificity of the reagent is not objectionable, as colour is developed only with the cellulose resins. Cellulose nitrate interferes and cannot be determined by this method. L.T.W.

Measurement of the pH of Fibrous Collagen in Aqueous Media
D. M. G. Armstrong

J. Physiol., 135, 26 P (1956):
J. Soc. Leather Trades Chem., 41, 436 (Dec. 1957)
By means of the cell— $Hg/HgCl_2$: saturated KCl solution: fibrous collagen: equilibrium solution: glass electrode— the pH of fibrous collagen may be obtained. Both the isoelectric and the iso-ionic points may be determined.

C.J.W.H.

PATENT

Determining Textile Characteristics
U.S. Secretary of Agriculture *USP* 2,752,781
Apparatus in which the sound produced by rubbing samples of fibre, ya·n or fabric is utilised as an index of the characteristics of the sample, e.g. its handle, resilience, etc. C.O.C.

APPOINTMENTS etc

Advertisements relating to APPOINTMENTS VACANT, APPOINTMENTS WANTED, and MISCELLANEOUS ITEMS are invited for insertion on this page. Advertisements of Appointments Wanted are gratis to members, but must not exceed twenty-four words.

All inquiries relating to Advertisements should be addressed to THE GENERAL SECRETARY, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE.

Replies may be addressed Box —, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE, where all communications relating to these Advertisements are treated in strict confidence.

APPOINTMENTS VACANT

THE MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY
(Faculty of Technology in the University of Manchester)
Appointment of
LECTURER IN TEXTILE CHEMISTRY

APPLICATIONS are invited for a Lectureship in Textile Chemistry in the College with the title and status of Lecturer in the University of Manchester.

Candidates should be Honours graduates in Physics or Chemistry and will be expected to carry out research on physical, physico-chemical or chemical aspects of Textiles for which good facilities are available.

Salary— according to qualifications and experience on scale £900 × £50—£1350 × £75—£1650. Superannuation under the F.S.S.U. Children's allowances.

Conditions of appointment and form of application may be obtained from the Registrar, The Manchester College of Science and Technology, Manchester 1. The last date for the receipt of applications is Saturday, 31st May 1958.

BRADFORD INSTITUTE OF TECHNOLOGY
(College of Advanced Technology)
Principal— E. G. Edwards, B.Sc., Ph.D., F.R.I.C.

APPLICATIONS are invited for the post of Lecturer in Technology of Dyeing. Applicants for the post should have had industrial experience, preferably in connection with production, in development work or research, and should be qualified to conduct original work in some branch of the subject. Teaching experience at an advanced level would be an advantage.

The commencing salary will be in accordance with the Burnham Technical Award, namely, £1200 to £1350 per annum. Previous industrial or research experience at a suitable level may be taken into account in fixing the commencing salary.

Further particulars of the appointment and forms of application may be obtained from the Principal, Institute of Technology, Bradford 7.

W. H. LEATHEM
Clerk to the Governors

CITY OF BRADFORD CONDITIONING HOUSE
TEXTILE CHEMIST

APPLICATIONS are invited for this superannuable post from suitably qualified candidates. Duties involve the chemical testing of textile materials of all types from fibre to finished products. Candidates should have a sound practical experience of such work preferably including ability to deal with the investigation of defective textiles. Preference will be given to candidates holding a University degree or the Associateship of the Royal Institute of Chemistry or other appropriate qualifications.

Salary will be in accordance with Grade APT.III (£845 to £1025 p.a.). Commencing salary may be fixed according to qualifications and experience.

Applications accompanied by names of two referees and endorsed "Textile Chemist" should reach me by Saturday, 7th June 1958.

W. H. LEATHEM, *Town Clerk*
Town Hall, Bradford

TEXTILE TECHNOLOGIST required in north London laboratories of growing public company manufacturing plastics coated fabrics. Age 28–35, with A.T.I. or equivalent qualifications. Applicants should possess an inquiring mind and an aptitude for development work and must have had several years industrial experience in textile finishing. A working knowledge of synthetic resins would be an advantage. Applications in writing giving full details and experience to the Technical Director, Staflex Company Limited, Clavering Estate, Montagu Road, London, N.9.

AWARDS AND SCHOLARSHIPS

THE UNIVERSITY OF LEEDS
Charles Brotherton Scholarship in Colour Chemistry

APPLICATIONS are invited for the above Scholarship of an annual value of £125, provided to enable suitably qualified students to enter upon a course of study leading to an Honours degree in the Department of Colour Chemistry and Dyeing. The Scholarship is tenable for three or four years and in cases where the candidate reaches the required standard, may be supplemented by an additional award (a supplemental State Scholarship) by the Ministry of Education.

Further particulars and forms of application may be obtained from the Registrar, The University, Leeds 2, to whom application should be made before 30th June 1958.

THE UNIVERSITY OF LEEDS
Department of Colour Chemistry and Dyeing
Entrance Awards

APPLICATIONS are invited for the following entrance awards tenable in the Department of Colour Chemistry and Dyeing— *Gunnell Studentships* of the value of £50 a year.

Other things being equal, preference will be given to students who have resided or whose parents have been resident in the West Riding of Yorkshire and who would otherwise find difficulty in entering upon a degree course.

Matthews Scholarship in Colour Chemistry, normally of the value of £100 a year.

Where a candidate reaches the required standard, the scholarship may be supplemented by the award of a supplemental State Scholarship by the Ministry of Education.

Applications should reach the Registrar, The University, Leeds 2, from whom further particulars and application forms may be obtained, not later than 30th June 1958.

MISCELLANEOUS

STRONG all cane lidded Hampers, hide bound— hardwood runners, splendid job, as new, half-price or less, depending on quantity. Size 22 × 20 × 21 in. inside— rectangular. Pattison, 218 Siddals, Derby. Telephone 45249.

WANTED one copy of "Manual of Dyeing", by E. Knecht & C. Lawson, published by Messrs. Charles Griffin & Co., 42 Drury Lane, London. Particulars to Allen C. Sugden, Royds Hall, Low Moor, near Bradford, Yorkshire.

NEW MEMBERS

Persons desirous of joining the Society as Ordinary Members or Junior Members can obtain Application Forms from the General Secretary, or from the Honorary Secretary of any Section of the Society

Adams, N. S., 50 Bakers Lane, Streetly, Sutton Coldfield, Warwickshire

Barclay, J., 28 Lismore Drive, Glenburn, Paisley, Renfrewshire

Coates, E., 236 Poplar Grove, Great Horton, Bradford 7, Yorkshire

Dawson, J., 3 Regent Park, Lurgan, Northern Ireland

Gandhi, N., College of Science and Technology, Sackville Street, Manchester 1

Higginbotham, R. S., 26 Stanley Road, Heaton Moor, Stockport, Cheshire

Jones, H. E. B., Shell Chemical Co. Ltd., Warwick Chambers, 14/20 Corporation Street, Birmingham 2

Lauchenauer, A., Raduner & Co. Ltd., Horn TG., Switzerland

MacNeil, E. S., 131 Terrace Drive, Toccoa, Georgia, U.S.A.

Major, S. J., 18 Tudor Avenue, Hampton, Middlesex

Marathe, A. B., 105 Withington Road, Whalley Range, Manchester 16

Moore, M. E., 58 Bedford Road, Great Barford, Bedfordshire

Murdoch, W. M., 10 Cheviot Road, Potterhill, Paisley, Renfrewshire

Pels, W., Ga. Institute of Technology, Box 4532, Atlanta, Ga., U.S.A.

Porter, F., North Manchester Golf Club, Rhodes House, Middleton, Lancashire

Richardson, H. H., Shell Chemical Co. Ltd., 105/109 Strand, London, W.C.2

Rigby, T. P., 38 Lynton Drive, Heaton, Bradford 9, Yorkshire

Sharp, F. D. H., The Geigy Co. Ltd., 14 Alfred Street, Belfast, Northern Ireland

Shaw, A., 12 Melville Street, Glasgow 8.1, Scotland

Shaw, C., 76 Thomas Street, Whitworth, near Rochdale, Lancashire

Stern, Dr. H., Ciba Limited, Basle, Switzerland

Stubbs, K. W., 14 Wellstone Drive, Bramley, Leeds 13, Yorkshire

Ukachuku, N., c/o Okezie Kanu, W.A.A.C., Radio W/S, Ikeja, Nigeria

Williams, P. J., 12 Chester Terrace Mews, London N.W.1

Wilson, C. T., 6 Stray View, Leeds Road, Harrogate, Yorkshire

Wiseman, L., British Rayon Research Assoc., Heald Green, near Manchester

ADDRESSES WANTED

Abrams, W. G., *formerly of* P.O. Box 3429 Ga. Tech., Atlanta, Ga., U.S.A.

Bromby, N. G., *formerly of* 170 Palatine Road, West Didsbury, Manchester

Cameron, M. C., *formerly of* 11 Thirlmere Gardens, Belfast, N. Ireland

Ciprut, J. V., *formerly of* Technical College, Dyeing Dept., Bradford, Yorkshire

Desmond, J. J., *formerly of* 1416 Molcomb Road, Huntington Valley, Pa., U.S.A.

Drzewicki, M., *formerly of* Flat 2, 11 Rectory Road, West Bridgford, Nottinghamshire

Gale, R. A., *formerly of* 32 Wordsworth Street, Hapton, near Burnley, Lancashire

Harris, A., *formerly of* "Laurel Bank", 36 High Street, Newton-le-Willows, Lancashire

Harvey, H. C., *formerly of* 77 Edinburgh Road, Congleton, Cheshire

Heaton, R., *formerly of* 142 Browning Road, Manor Park, London E.12

Hollis, D. J., *formerly of* "Kinder Spur", Hayfield, Stockport, Cheshire

Hubler, B., *formerly of* Park Hotel, Oak Avenue, Manningham, Bradford 8

Jackson, J. B., *formerly of* 36 Arden Road, Crumpsall, Manchester 8

Jliadis, S., *formerly of* Nottingham and District Technical College, Shakespeare Street, Nottingham

Kabil, R., *formerly of* Sefitex and Company, Mataria Street, Zeitoun, Cairo, Egypt

Kothawala, Amin A., *formerly of* 36 Briarwood Drive, Wibsey, Bradford 6

Kubba, S., *formerly of* 10 Malone Road, Belfast, N. Ireland

Le Bek, I. A. G., *formerly of* 8 Lad-Hill Lane, Greenfield, near Oldham, Lancashire

Lovatt, J., *formerly of* 9 Duchy Drive, Heaton, Bradford, Yorkshire

Maschas, L., *formerly of* 43 St. John's Road, Huddersfield

Midgley, F. B., *formerly of* "Clova", 57 Jeremy Lane, Heckmondwike, Yorkshire

Moody, L. E., *formerly of* 67 Wilfrid Street, Valleyfield, Quebec, Canada

Musselwhite, A. G., *formerly of* 6 Margery Terrace, Gummersdale, Carlisle

Oxley, R., *formerly of* 27 Hayling Road, Sale, Manchester

Ramadan, A. S., *formerly* c/o Beida Dyers, Dyeing Department, Alexandria, Egypt

Rahman, S. M. K., *formerly of* Lock View Hall, 1025 Gt. Western Road, Glasgow

Richardson, D., *formerly of* 139 Laund Road, Salendine Nook, Huddersfield

Shane, H. J. S., *formerly of* 66 Portallo Street, Castlereagh Road, Belfast, N. Ireland

Slater, W. K., *formerly of* 27 Hope Road, Sale, Cheshire

Smith, L., *formerly of* 80 Fair View Road, Bacup, Lancashire

Stamires, D., *formerly of* 9 Shaw Lane, Leeds 6

Troxler, M. D., *formerly of* Georgia Institute of Technology, Box 680, Ga. Tech., Atlanta, U.S.A.

Tsien, P. C., *formerly of* 1332 Tenan Road, Shanghai, China

Wahba, F. S., *formerly* c/o Beida Dyers S.A.E., P.O. Bag., Alexandria, Egypt

Wailes, N. T., *formerly of* "Hamewith", 4 Kingsway Terrace, Dundee, Scotland

Walker, T. H., *formerly of* J. L. Stifel & Sons Inc., 339 Main Street, Wheeling, W. Va., U.S.A.

Zwicky, A. M., *formerly of* 23 West-Leight Street, Crumpsall, Manchester 9

MEMBERS' CHANGES OF ADDRESS

Bennett, A., *formerly of* 1 Cranworth Street, Stalybridge, Cheshire, *to* c/o B.I.P. Chemicals Ltd., 79 Mosley Street, Manchester 2

Blackburn, Alan, *formerly of* 47 Carlinghow Lane, Batley, Yorkshire, *to* 20 Horner Crescent, Carlinghow Lane, Batley, Yorkshire

Blakey, G. B., *formerly of* North Lodge, Stanely Road, Paisley, Scotland, *to* Hilos Rimac S.A., Lima, Peru

Brown, S. H., *formerly of* 2 Whitehall Lane, Llanfrecha, Cwmbran, Monmouthshire, *to* "Highfield Stile", Belgrave Road, Abergavenny, Monmouthshire

Cabral, Eng. Joao de Oliveira, *formerly of* Rua Moreira Da Sa, 141, Porto, Portugal, *to* Rua De Cedofeitra, 347-2-D, Porto, Portugal

Clarkson, J. P., *formerly of* 28 The Orchard, Winchmore Hill, London N.21, *to* 36 The Orchard, Winchmore Hill, London N.21

Edge, E. N., *formerly of* 117 Crompton Way, Bolton, Lancashire, *to* 2 Brookside Road, Bolton, Lancashire

Empson, H. B., *formerly of* 22 Hirst Wood Road, Shipley, Yorkshire, *to* 3 Westfield Grove, Wrose, Shipley, Yorkshire

Evans, B., *formerly of* 13 Carriagehill Drive, Paisley, Scotland, *to* 47 Lomondshire Avenue, Clarkston, Renfrewshire, Scotland

Fisher, W. J., *formerly of* 4 Lowswork Cottages, Perthshire *to* 5 Lowswork Cottages, Almondbank, Perthshire

Fornelli, D., *formerly of* Via Taluchir 20, Turin, Italy, *to* Via Privata Biancardi 4, Milano, Italy

Fox, W., *formerly of* 9 Belmont Road, Sale, Cheshire, *to* 4 Banbury Road, Alkrington, Middleton, Lancashire

Ghoroury, Dr. M. S. El, *formerly of* 20 Abdel Rahman El Barkouky Str., Cairo (Manyal), Egypt, *to* 6 Morison Street, Saba Pacha, Alexandria, Egypt

Heaton, James, *formerly of* Tame House, Reddish Vale, Stockport, Cheshire, *to* 11 Chester Avenue, Duxbury, Chorley, Lancashire

Holt, Frank, *formerly of* 28 Pennington Street, Walshaw, Bury, Lancashire, *to* 33 St. Anne's Street, Bury, Lancashire

Jackson, T., *formerly of* "Fairholme", 24 Curzen Lane, Alvaston, Derbyshire, *to* 16 Follingworth Road, off Solway Road, Batley, Yorkshire

Johnson, R. F., *formerly of* Georgia Institute of Technology, Atlanta, Ga., U.S.A., *to* Research Dept., Dye Section, The Dow Chemical Company, Warwick, Va., U.S.A.

Jowett, A. M., *formerly of* 19 Pleasant Street, Sowerby Bridge, Yorkshire, *to* 6 Dam Head Road, Sowerby Bridge, Yorkshire

Mackay, C., *formerly of* 27 Leyland Street, Accrington, Lancashire, *to* 25 Brookfield Avenue, Ainsworth, Bolton, Lancashire

Mackie, W. T., *formerly of* 2 Barnfield Crescent, Exeter, Devon, *to* Santral Dikis Sanayii T.A.S., P.K. 193, Istanbul, Turkey

Menkart, J., *formerly of* Textile Research Institute, Princeton, N.J., U.S.A., *to* Harris Research Laboratories, 1246 Taylor Street, N.W., Washington 11, D.C., U.S.A.

Schofield, J., *formerly of* 87 St. Enoch's Road, Wibsey, Bradford 6, *to* "Norwood House", 53 Wyke Lane, Oakenshaw, Bradford

Smith, Miss E., *formerly of* Cliffe House, Bruntcliffe, near Leeds, *to* Flat 16, Foxhill, Weetwood Lane, Leeds 16

Smith, F., *formerly of* Cliffe House, Bruntcliffe, near Leeds, *to* Flat 16, Foxhill, Weetwood Lane, Leeds 16

Smith, S., *formerly of* 25 Villas Road, Ambergate, Derbyshire, *to* 9 Rock House, Cromford, near Matlock, Derbyshire

Taylor, K., *formerly of* 129 Napier Street, Nelson, Lancashire, *to* Chadkirk Dyeworks, Romiley, Stockport, Cheshire

Wainwright, P., *formerly of* 13 Regent Park Terrace, Leeds 6, Yorkshire, *to* Leeds University Union, University Road, Leeds 2, Yorkshire

PUBLICATIONS AVAILABLE FROM
THE SOCIETY OF DYERS AND COLOURISTS
DEAN HOUSE 19 PICCADILLY BRADFORD 1 YORKSHIRE

JOURNAL OF THE SOCIETY OF DYERS AND COLOURISTS
(published monthly) Price to Non-members per annum £5 5s

THE THEORY AND PRACTICE OF WOOL DYEING (Second Edition)
By C L BIRD *Price* 15s

IDENTIFICATION OF DYES ON TEXTILE FIBRES AND DETECTION OF METALS IN FIBROUS MATERIALS, DYES, AND ORGANIC PIGMENTS
(Second Edition)
By ELLIS CLAYTON *Price* 10s 6d

REPORTS OF THE COMMITTEES ON THE DYEING PROPERTIES OF DIRECT COTTON, VAT, AND WOOL DYES
Price 5s

RECENT ADVANCES IN THE COLOURING OF MAN-MADE FIBRES
Proceedings of a Symposium held at Buxton in September 1957
Price £2

BLEACHING, DYEING, AND FINISHING TO-DAY
Proceedings of a Symposium held at Portrush, Northern Ireland in September 1955
Price £1 10s

TEXTILE PRINTING
Proceedings of a Symposium held at St. Annes-on-Sea in September 1953
Price £1 10s

THE TINCTORIAL ARTS TO-DAY
Proceedings of a Conference held at Harrogate in September 1951
Price 15s Members £1 5s Non-members

PHOTOCHEMISTRY IN RELATION TO TEXTILES
Proceedings of a Symposium held at Harrogate in September 1949
Price £1 Members £1 10s Non-members

STANDARD METHODS FOR THE ASSESSMENT OF THE COLOUR FASTNESS OF TEXTILES
(Third Report of the Fastness Tests Co-ordinating Committee)
Price 7s 6d

LABORATORY COURSE IN DYEING
By C H GILES *Price* 17s 6d (*plus* 8d *postage*)

REVIEW OF TEXTILE PROGRESS
Volume I 1949 £1 Volume II 1950 £1 5s

Volume III 1951 Volume IV 1952 Volume V 1953
£1 15s *each* (£1 8s to S.D.C & T.I Members)

Volume VI 1954 £1 17s 6d (£1 10s to S.D.C & T.I Members)

Volume VII 1955 Volume VIII 1956
£2 2s *each* (£1 13s to S.D.C & T.I Members)

(postage extra on each volume)

A S D C EXAMINATION
QUESTION PAPERS AND REPORT OF THE DIPLOMAS EXECUTIVE SUB-COMMITTEE
1954 1955 1956 1957 *Price* 1s *each*

INDEX TO ADVERTISERS